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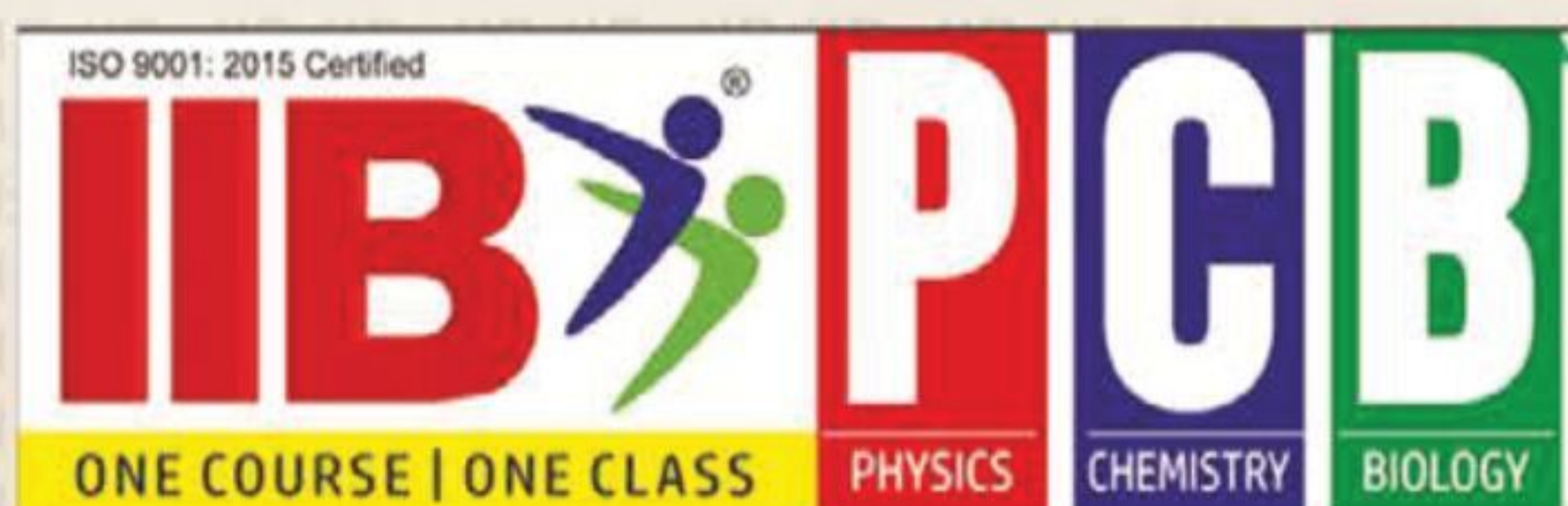
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The logical side of Physics

Amazon Academy's Physics teacher Ashish Gupta talks about his perspectives on how to tackle Physics for JEE & NEET syllabus.

Ashish Gupta had two passions in his life: Physics and teaching. He made the most of both and decided to become a teacher. Nine years on, Ashish Sir, as he is popularly known to his students, is happy he decided to act on his first two loves. As Amazon Academy's Physics faculty, Ashish Sir explains how Physics is the most practical subject among the all JEE subjects. He says Physics needs a fair amount of logical understanding of concepts and significant practice. Application is as important as theory, he emphasizes in this informative tête-à-tête.

Take us through your educational years Ashish Sir!

Sure. I did my schooling till 10th from Jodhpur, Rajasthan. My favorite subject kept fluctuating between Physics and Maths till 10th standard. I went to Kota to prepare for JEE for a couple of years. In 11th standard, I understood that while Maths was a comprehensive subject, Physics made me happy. It had a good balance of logic, understanding and numerical. In 12th, I cleared the JEE in my first attempt and went to IIT Bombay to pursue B.Tech. in Mechanical Engineering before graduating in 2009.

What did you do after that?

After my graduation, I got placed in a company where we used to trade derivatives. I did that for a couple of years but I was always passionate about teaching. Physics always excited me as a subject. So, I decided to act upon my passion and in 2012, joined FIITJEE as a teacher. I also taught at IITian's Pace in Nagpur for three years. Then I was in Indore for the last three years at Allen Career Institute, before joining Amazon Academy. I have been a teacher for the last nine years now.

Tell us what are the topics a student should study in JEE & NEET?

I would say that Optics and Modern Physics are the topics which are important. They are concise in nature; they might not be exhaustive but the number of questions that come from those topics are quite high. Apart from that, Electromagnetic Induction, Alternating Current, and Magnetism also contribute significantly to the number of questions that you see in the papers. All of these are Class 12th topics. For 11th, Thermodynamics is a very good topic — it's a concise topic but then again, students tend to neglect it. The number of questions that come from Thermodynamics is quite high.

For JEE Main, the same topics are high priority. I would also add Semiconductors, Communication, Polarization, Diffraction – topics that appear only in Main. JEE tends to ask questions from these topics every year and the level of questions is also not

that high. So, if students devote just even a day in learning these topics, they tend to do well. In turn, this helps them score better.

Which books should the students refer to?

There are certain standard books that everybody studies from. One of them is Concept of Physics by H.C. Verma. It's a good book for basic understanding. For basic concepts, I would recommend a book by Resnick, Halliday, and Walker i.e. Principles of Physics. This is again a book which focuses on the concepts.

As for problem solving and practice purposes, I would say H.C. Verma is a good book. Apart from that, we have our own Amazon Academy platform that deals with questions on each topic as well as part and full tests that are available for free. I can vouch that the level of these questions is amazingly good. One more source which is usually underrated but very reliable is the previous years' questions. So, the last 40-45 years of question banks should be accessed. This helps the students check their understanding of topics. It's an absolute must.

What about revision? Any tips on that?

You must remember that not everyone who practices gets good marks. I cannot emphasize enough on revisiting and revising previous topics. Let me explain: Suppose you have learnt a topic today and you do not go through it for the next two months, there is a good chance that you will forget it. My recommendation is to solve at least 15 to 20 questions after two-three weeks. This will help you dust up on what you studied earlier. So, structure your academics in a way that you can engage in questions of the previous topics along with the current topics.

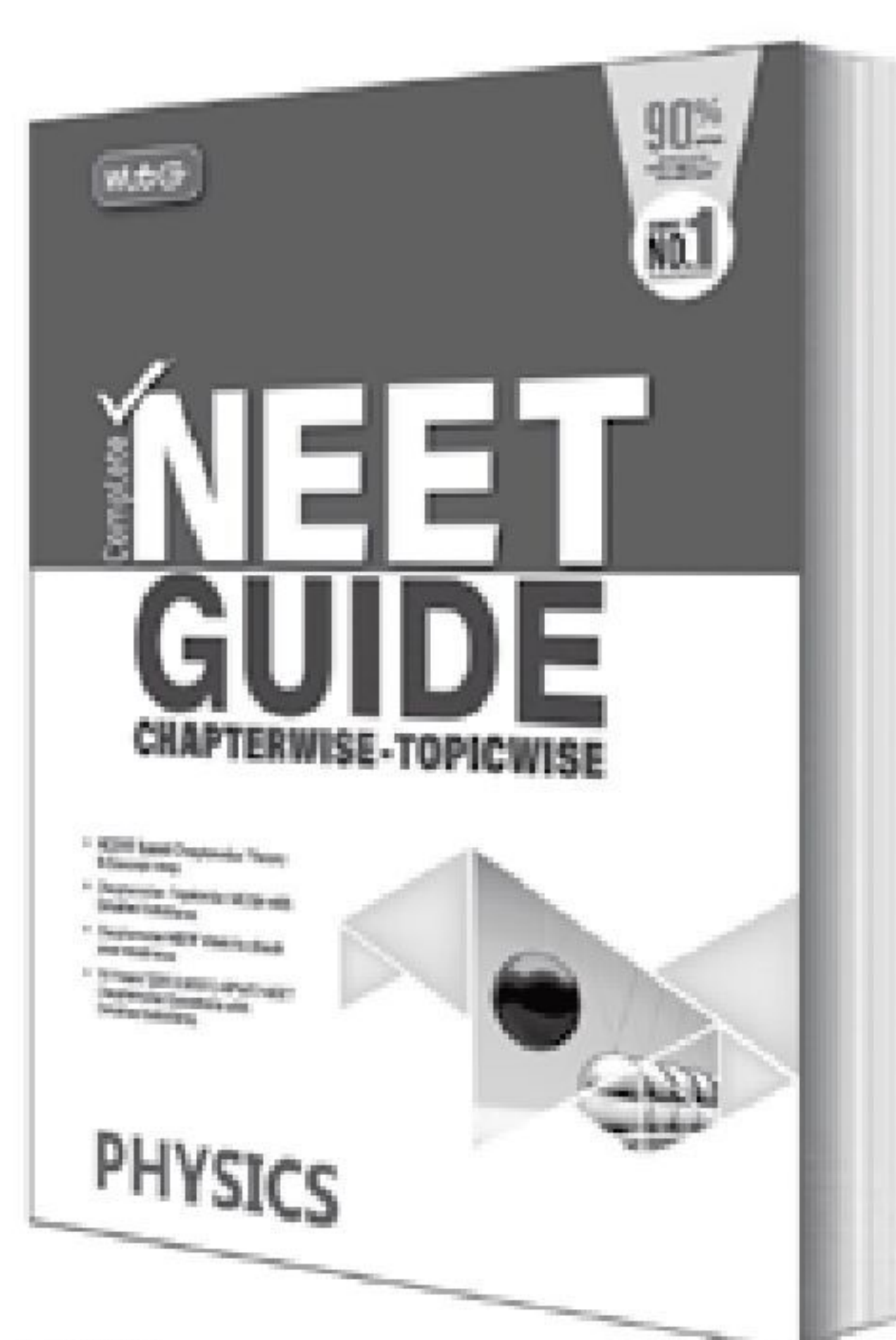
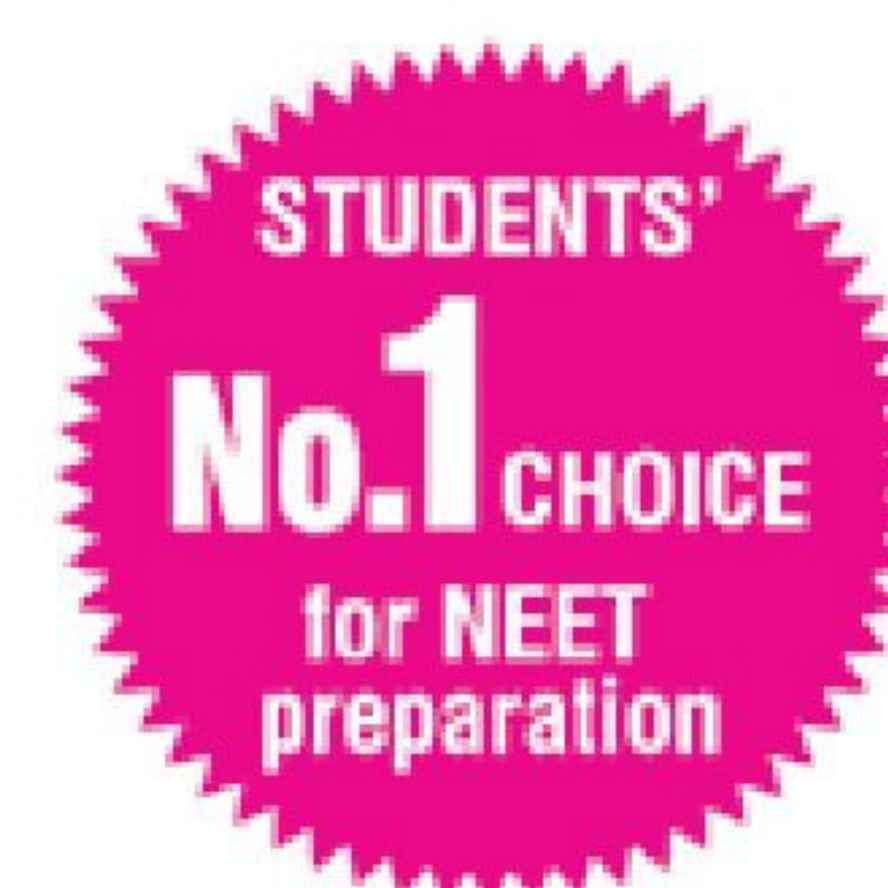
Anything else you would like to add?

See, there is a saying in Physics, 'Logic is Magic'. If you are a logical person, then you have a good chance of cracking Physics as a subject. But I also feel that we overemphasize on logic sometimes. Students feel that they must grasp a concept first, understand it, then implement it. It's not like that. I think the majority of students miss the trick by focusing too much on concepts and not working hard enough on their skill set. If you practice a lot in Physics, you will fall in love with the subject. You will realize that the questions are so practical. So be mentally ready to practice... practice hard.

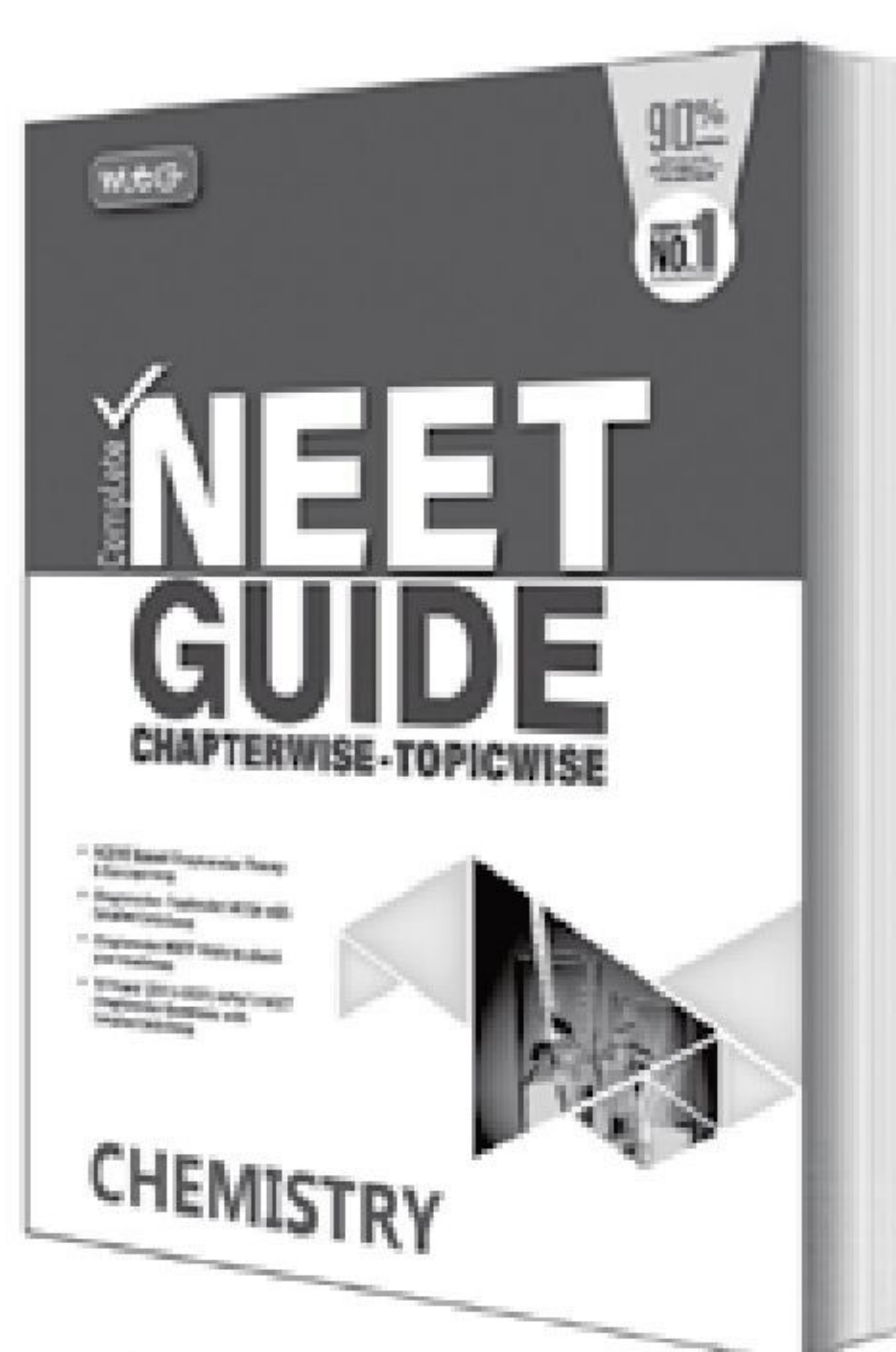
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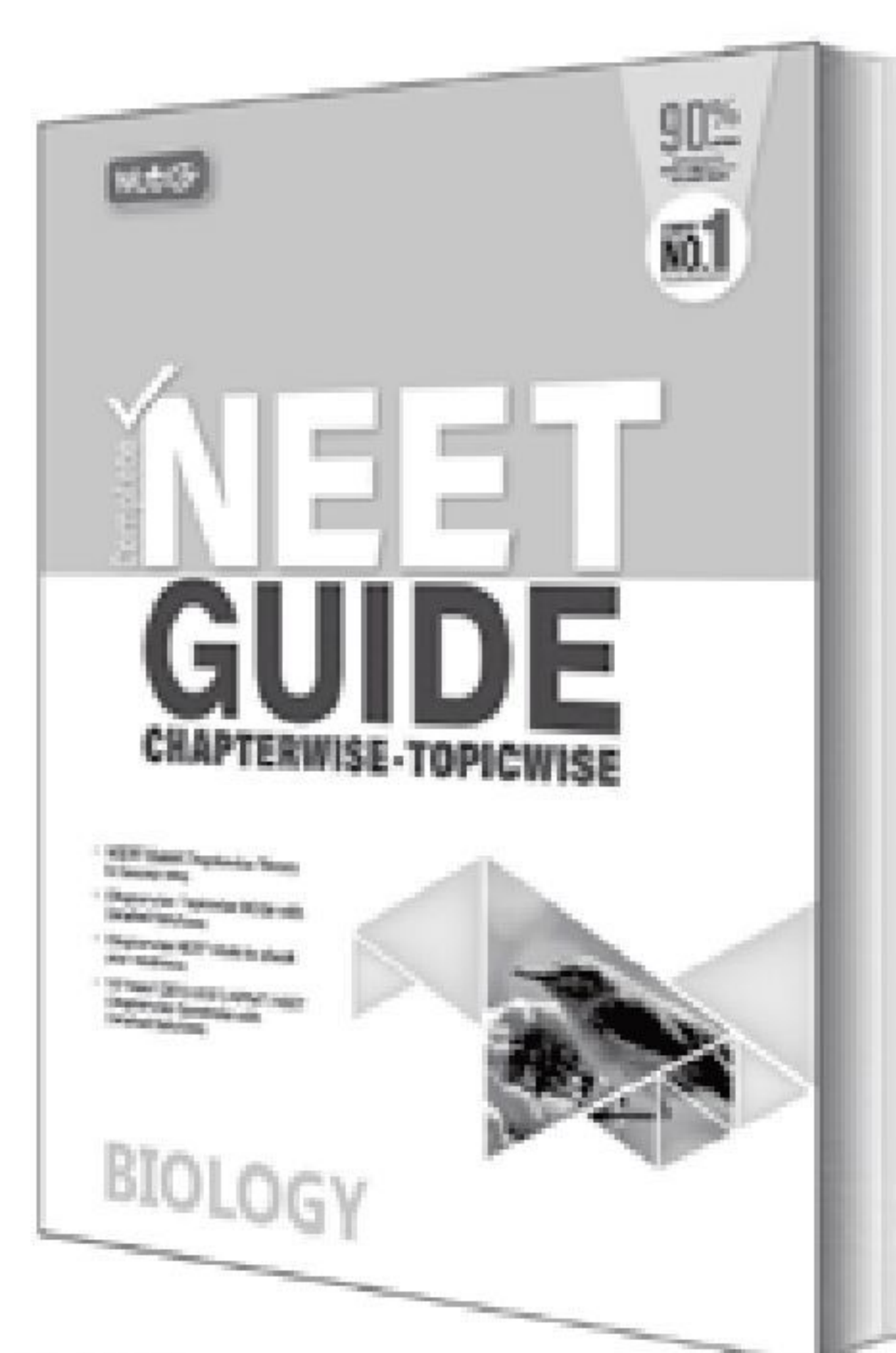
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HIGHLIGHTS:

- 100% NCERT based
- Comprehensive Chapterwise theory complemented with concept maps, flowcharts and easy-to-understand illustrations
- Last 10 years' questions (2012-2021) of AIPMT/NEET
- Chapterwise - Topicwise MCQs with detailed explanations and solutions
- Approx. 90% same or similar MCQs in NEET are from MTG NEET Books



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GET SET GO NEET

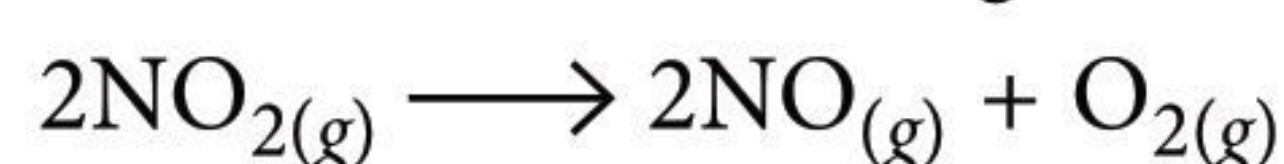


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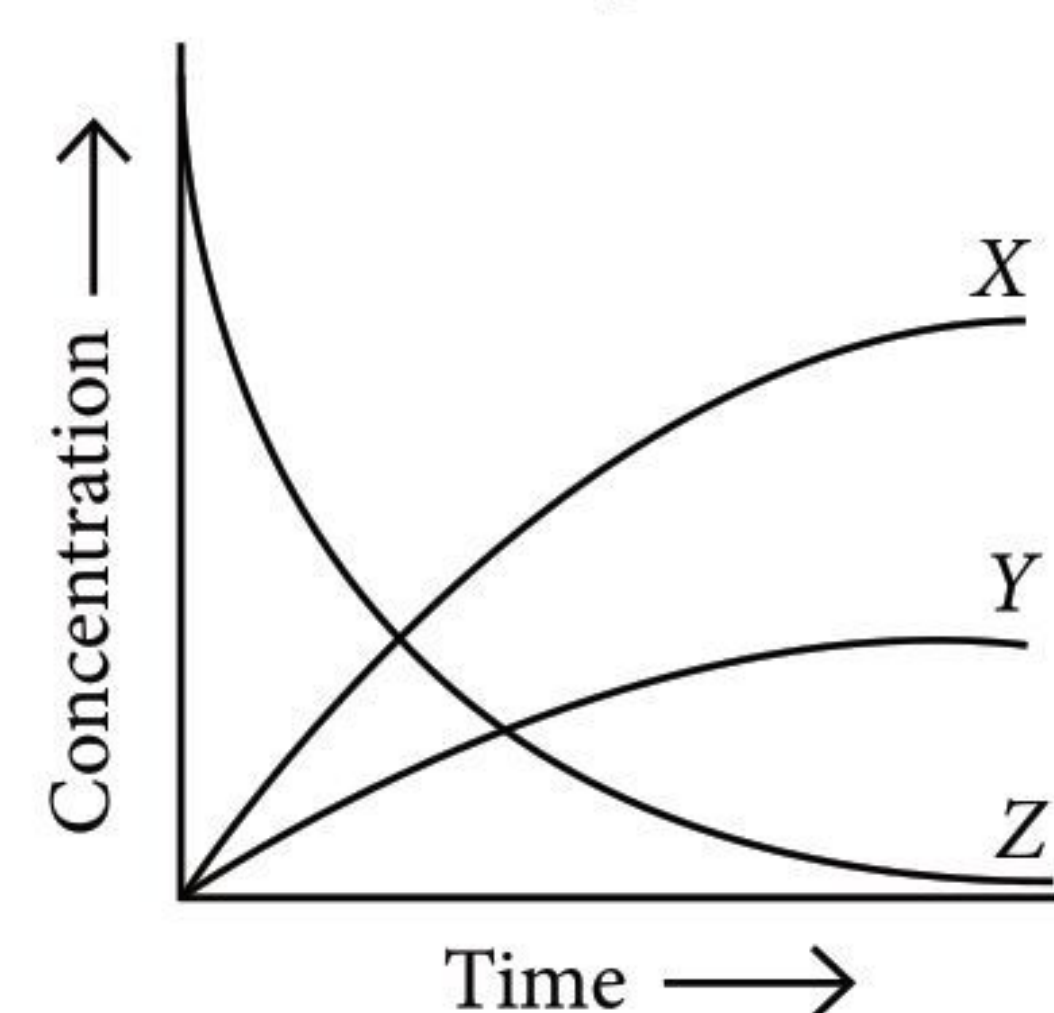
Practicing these MCQs help to strengthen your concepts and give you extra edge in your NEET preparation

- The number of water molecules present in a drop of water (volume 0.0018 mL) at room temperature is
 (a) 6.023×10^{19} (b) 5.023×10^{23}
 (c) 1.084×10^{18} (d) 4.84×10^{17}
- What is the maximum number of electrons in the all possible sub-shells for $n + l = 4$?
 (a) 8 (b) 6 (c) 12 (d) 16
- Which gas will liquefy easily (a and b are van der Waals' constants)?
 (a) Larger value of a and b
 (b) Smaller value of a but larger value of b
 (c) Smaller values of a and b
 (d) Larger value of a but smaller value of b
- Arrange the following in the order of increasing entropy:
 (A) 1 mol of $\text{H}_2\text{O}_{(s)}$ at 0°C and 1 atm pressure
 (B) 1 mol of $\text{H}_2\text{O}_{(l)}$ at 0°C and 1 atm pressure
 (C) 1 mol of $\text{H}_2\text{O}_{(l)}$ at 25°C and 1 atm pressure
 (D) 1 mol of $\text{H}_2\text{O}_{(l)}$ at 25°C and 0.8 atm pressure
 (E) 1 mole of $\text{H}_2\text{O}_{(v)}$ at 100°C and 1 atm pressure
 (a) $A < B < C < D < E$
 (b) $B < A < C < D < E$
 (c) $B < D < A < C < E$
 (d) $A < C < B < D < E$

- Consider the following reaction:



In the figure below, identify the curves, X, Y and Z associated with the three species in the reactions



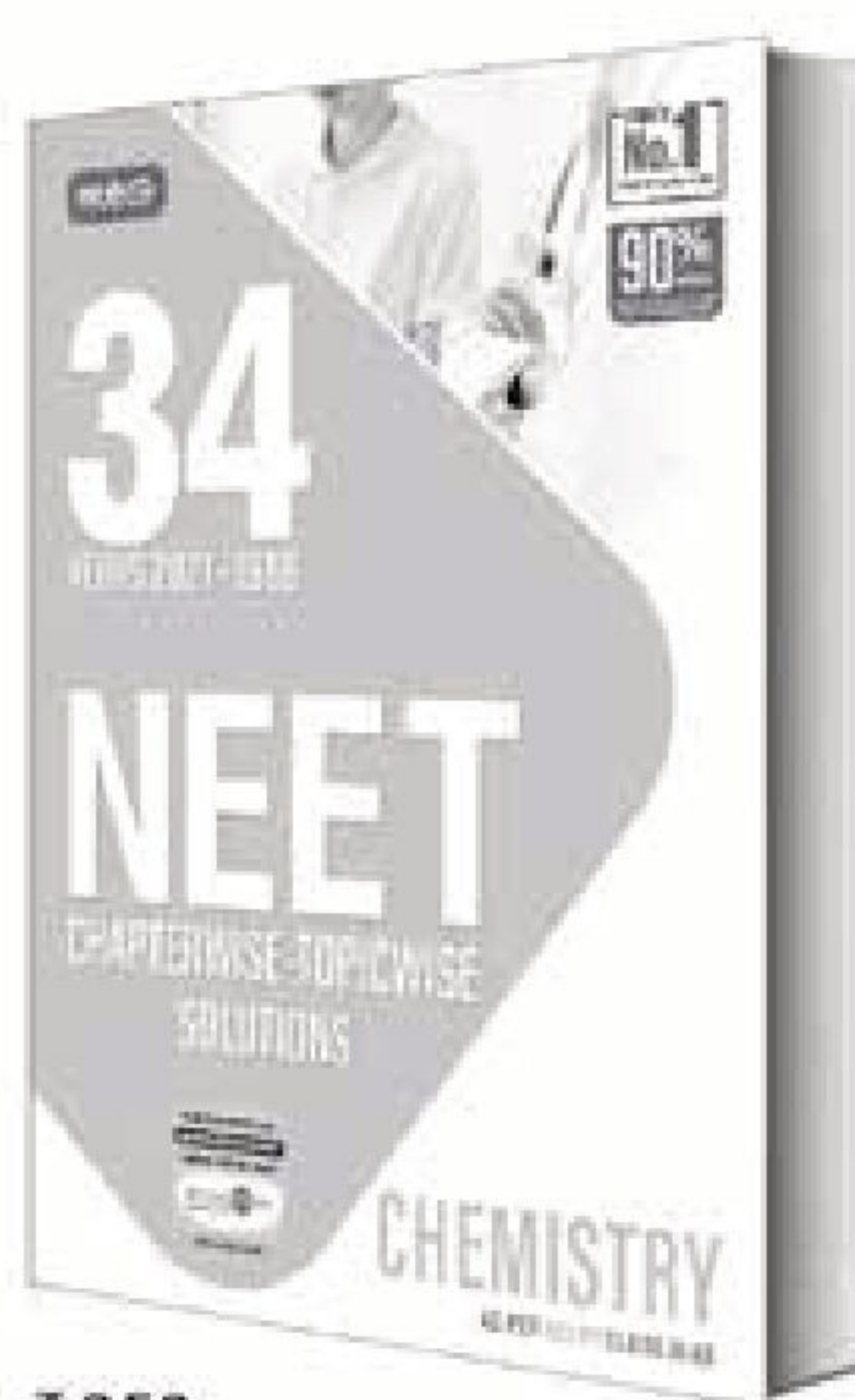
- (a) $X = \text{NO}$, $Y = \text{O}_2$, $Z = \text{NO}_2$
 (b) $X = \text{O}_2$, $Y = \text{NO}$, $Z = \text{NO}_2$
 (c) $X = \text{NO}_2$, $Y = \text{NO}$, $Z = \text{O}_2$
 (d) $X = \text{O}_2$, $Y = \text{NO}_2$, $Z = \text{NO}$
- In the balanced chemical reaction
 $\text{IO}_3^- + p\text{I}^- + q\text{H}^+ \longrightarrow r\text{H}_2\text{O} + s\text{I}_2$
 p , q , r and s respectively, correspond to
 (a) 5, 6, 3, 3 (b) 5, 3, 6, 3
 (c) 3, 5, 3, 6 (d) 5, 6, 5, 5
- The order of relative acidic strength of water, ammonia and acetylene is

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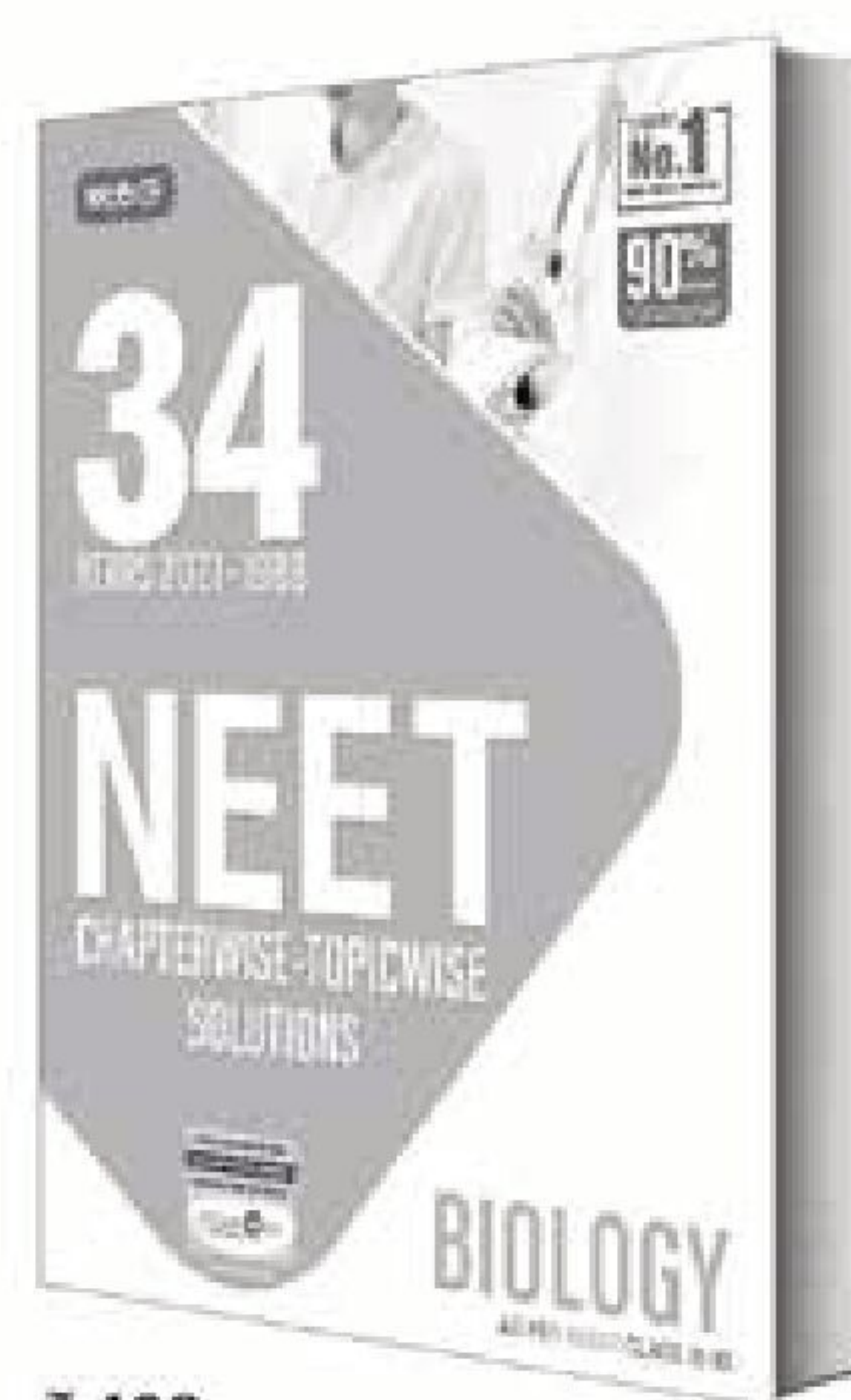
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HIGHLIGHTS:

- Chapterwise - Topicwise questions of last 34 years' (2021-1988) of NEET/AIPMT
- Chapterwise - Topicwise segregation of questions to help you assess the level of effort required to succeed
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- (a) water > ammonia > acetylene
- (b) ammonia > water > acetylene
- (c) water > acetylene > ammonia
- (d) acetylene > water > ammonia.

8. In carbon monoxide molecule, carbon and oxygen are linked by

- (a) only σ -bonds
- (b) only π -bonds
- (c) σ as well as π -bonds
- (d) none of these.

9. Which of the following species contains equal number of σ - and π -bonds?

- (a) $(\text{CN})_2$
- (b) $\text{CH}_2(\text{CN})_2$
- (c) HCO_3^-
- (d) XeO_4

10. Among CaH_2 , BeH_2 , BaH_2 , the order of ionic character is

- (a) $\text{BeH}_2 < \text{CaH}_2 < \text{BaH}_2$
- (b) $\text{CaH}_2 < \text{BeH}_2 < \text{BaH}_2$
- (c) $\text{BeH}_2 < \text{BaH}_2 < \text{CaH}_2$
- (d) $\text{BaH}_2 < \text{BeH}_2 < \text{CaH}_2$

11. The decreasing order of the second ionisation enthalpy of K, Ca and Ba is

- (a) $\text{K} > \text{Ca} > \text{Ba}$
- (b) $\text{Ca} > \text{Ba} > \text{K}$
- (c) $\text{Ba} > \text{K} > \text{Ca}$
- (d) $\text{K} > \text{Ba} > \text{Ca}$

12. Which of the following molecules has highest bond energy?

- (a) $\text{F}-\text{F}$
- (b) $\text{N}-\text{N}$
- (c) $\text{C}-\text{C}$
- (d) $\text{O}-\text{O}$

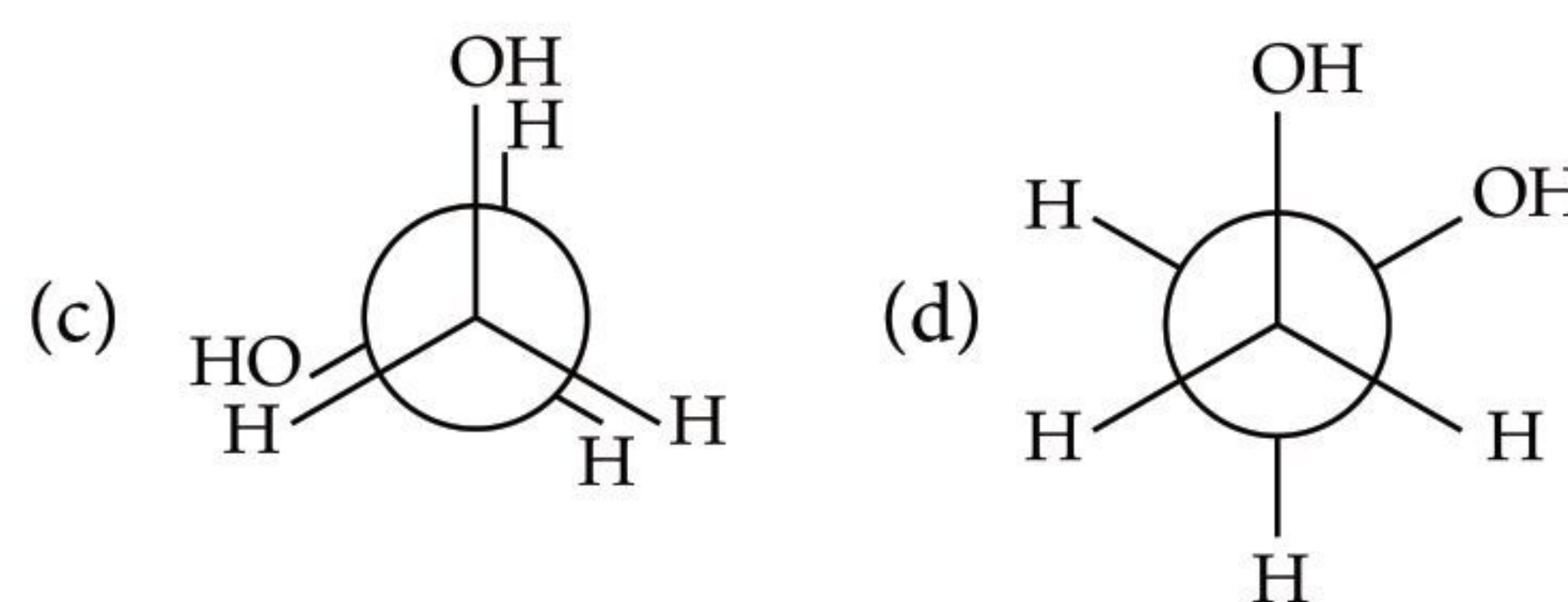
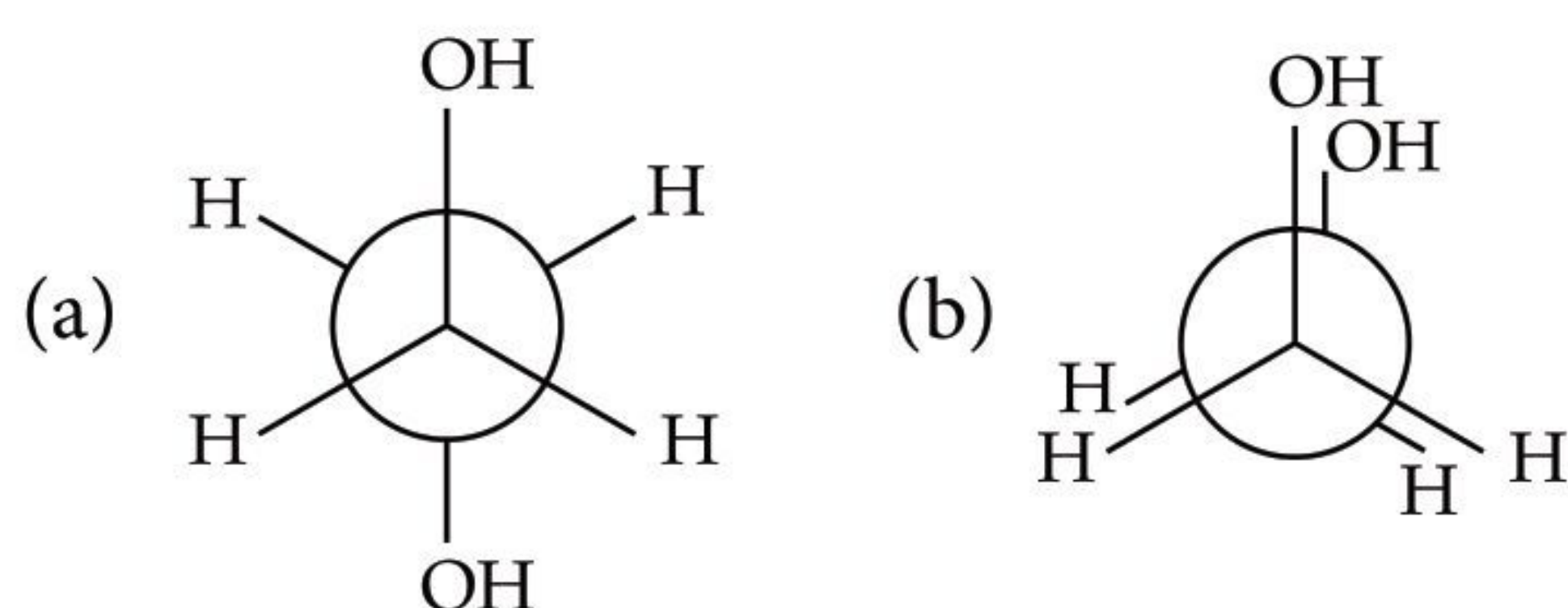
13. Which of the following sets does not represent isoelectronic species?

- (a) $\text{Ne}, \text{F}^-, \text{O}^{2-}$
- (b) $\text{Cl}^-, \text{Ar}, \text{K}^+$
- (c) $\text{S}^{2-}, \text{Br}^-, \text{Kr}$
- (d) $\text{Mg}^{2+}, \text{Na}^+, \text{Ne}$

14. When electric current is passed through an ionic hydride in molten state

- (a) hydrogen is liberated at anode
- (b) hydrogen is liberated at cathode
- (c) hydride ion migrates towards cathode
- (d) hydride ion remains in solution.

15. Which of the following conformers for ethylene glycol is most stable?



SOLUTIONS

1. (a): Weight of $\text{H}_2\text{O} = V \times d$

$$= 0.0018 \text{ mL} \times 1 \text{ g mL}^{-1} = 0.0018 \text{ g}$$

$$n_{\text{H}_2\text{O}} = \frac{0.0018}{18} = 10^{-4} \text{ mol}$$

$$\begin{aligned} \text{No. of water molecules} &= 6.023 \times 10^{23} \times 10^{-4} \\ &= 6.023 \times 10^{19} \end{aligned}$$

2. (a): $n + l = 4$

$$4 + 0 = 4s = 2$$

$$3 + 1 = 3p = 6$$

$$\text{Total} = 8$$

Maximum number of electrons = 8

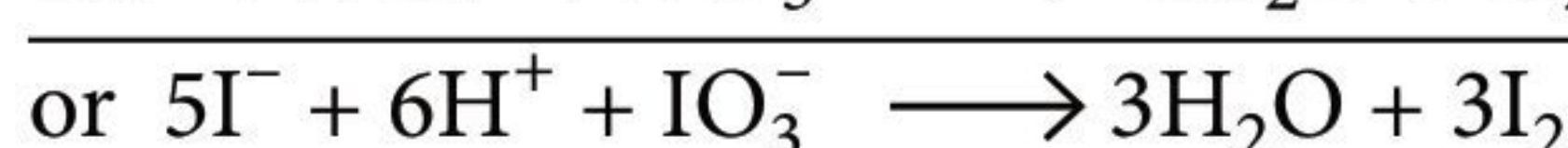
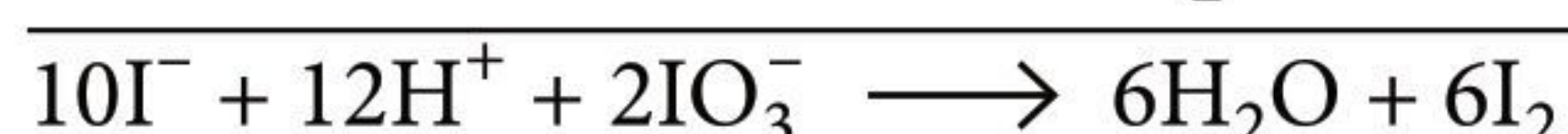
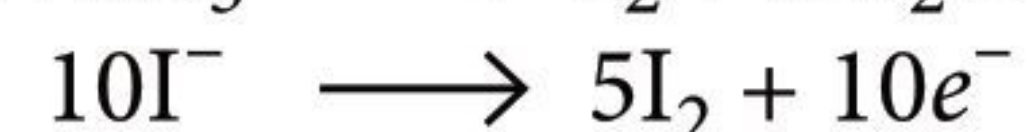
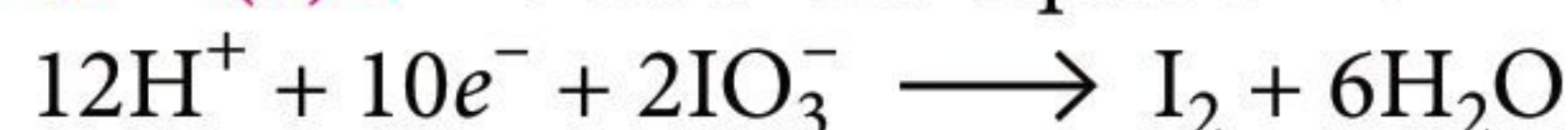
3. (d)

4. (a): Entropy of a molecule in gaseous state is greater than that of liquid state, which in turn greater than that in solid state.

Also, entropy decreases with increase in pressure and decrease in temperature.

5. (a): The concentrations of X and Y are increasing since they are products. For every 2 mol of NO_2 decomposed, 2 mol of NO and 1 mol of O_2 is formed. Hence, concentration of NO is greater than concentration of O_2 . This implies that X is NO and Y is O_2 . Since the concentration of reactant decreases with time, Z is NO_2 .

6. (a): The balanced equation is



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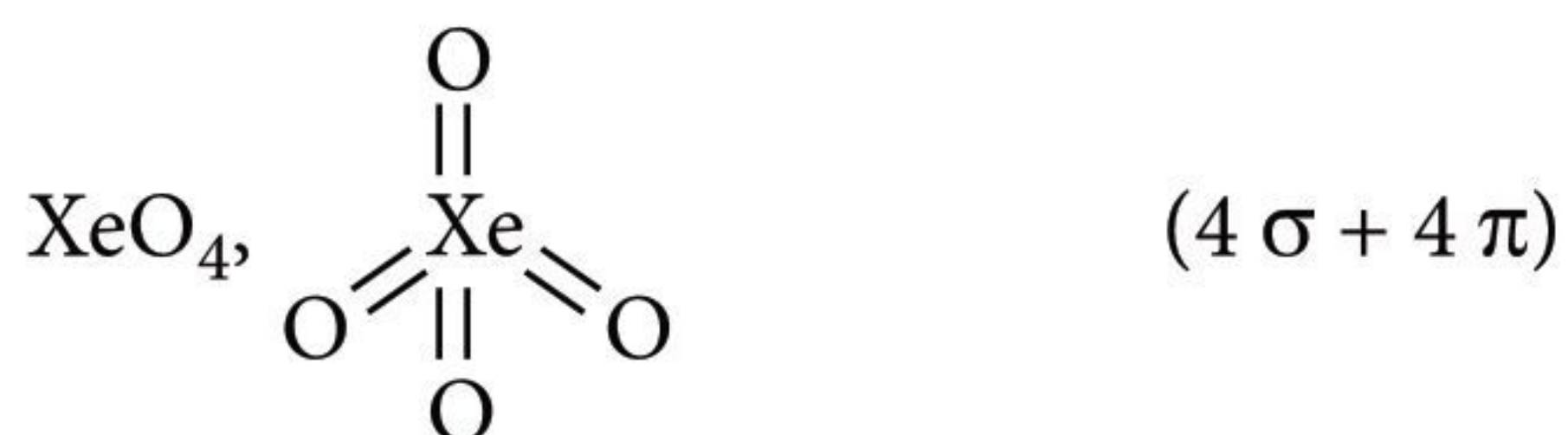
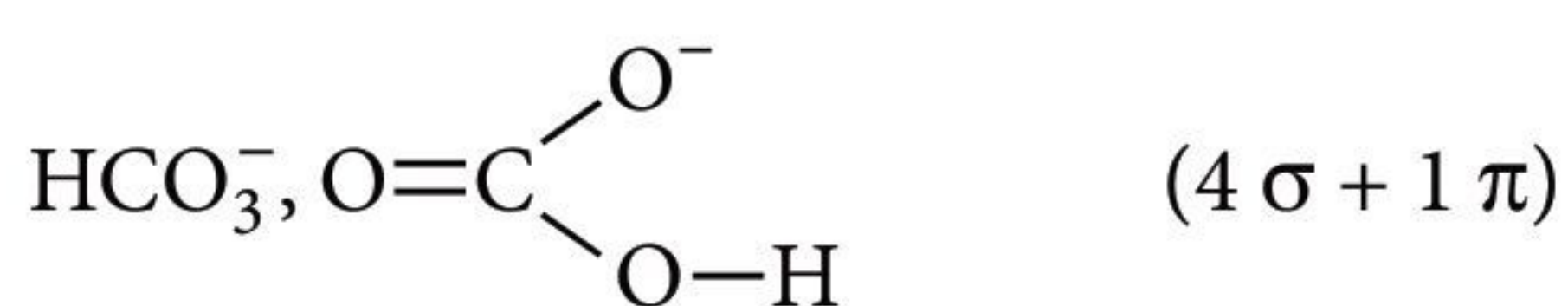
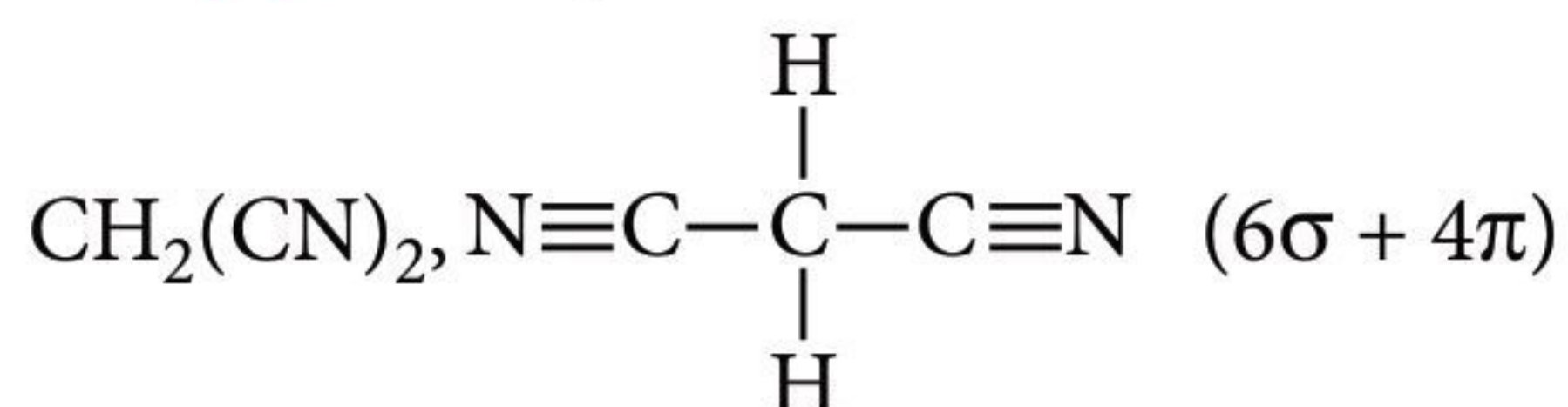
"Everyone is a genius. But if you judge a fish by its ability to climb a tree, it will live its whole life believing that it is stupid."

Albert Einstein

7. (c): For a compound to be strong acid, its conjugate base should be very stable. In case of H_2O , the negative charge on conjugate base (OH^-) is stable on more electronegative oxygen atom. In acetylene also, sp -hybridised carbon is enough electronegative to carry the negative charge on itself.

8. (c): In CO molecule, carbon and oxygen are linked by both σ and π bonds.

9. (d): $(\text{CN})_2$, $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ ($3\sigma + 4\pi$)



10. (a): $\text{BeH}_2 < \text{CaH}_2 < \text{BaH}_2$

On moving down the group, metallic character of metals increases. So, ionic character of metal hydrides increases. Hence, BeH_2 will be least ionic.

11. (a): $\text{K} > \text{Ca} > \text{Ba}$, IE_2 decreases down the group because of the increase in atomic size.

12. (c): The bond energies of $\text{F}-\text{F}$, $\text{C}-\text{C}$, $\text{N}-\text{N}$ and $\text{O}-\text{O}$ bonds are 158, 346, 163 and 146.4 kJ/mol respectively. Therefore, molecule of $\text{C}-\text{C}$ has the highest bond energy.

13. (c): $\text{Ne} \Rightarrow 10$, $\text{F}^- \Rightarrow 9 + 1 = 10$, $\text{O}^{2-} \Rightarrow 8 + 2 = 10$

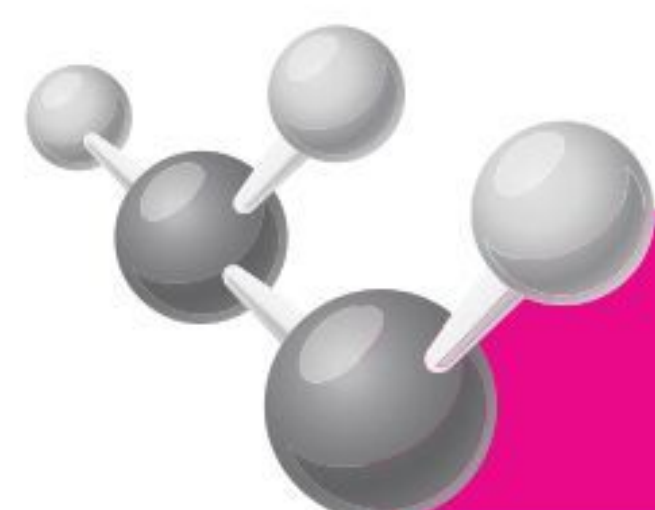
$\text{Cl}^- \Rightarrow 17 + 1 = 18$, $\text{Ar} \Rightarrow 18$, $\text{K}^+ \Rightarrow 19 - 1 = 18$

$\text{S}^{2-} \Rightarrow 16 + 2 = 18$, $\text{Br}^- \Rightarrow 35 + 1 = 36$, $\text{Kr} = 36$

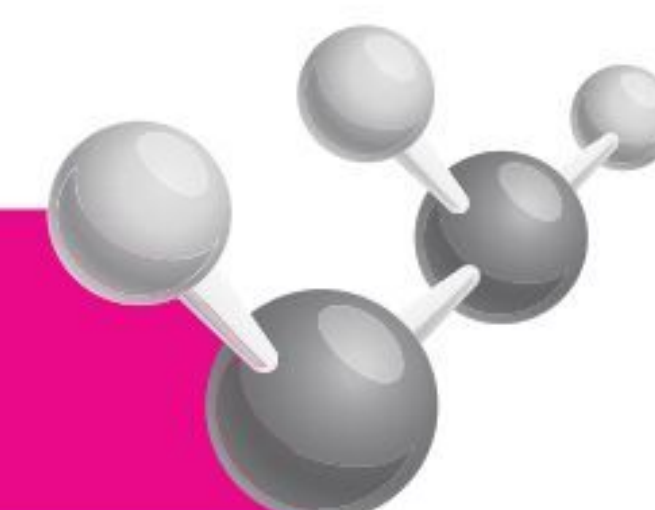
$\text{Mg}^{2+} \Rightarrow 12 - 2 = 10$, $\text{Na}^+ \Rightarrow 11 - 1 = 10$, $\text{Ne} = 10$

14. (a)

15. (d): The conformation (d) is most stable because of intramolecular H-bonding. This form is called gauche conformation.



3 Amazing Facts You Must Know



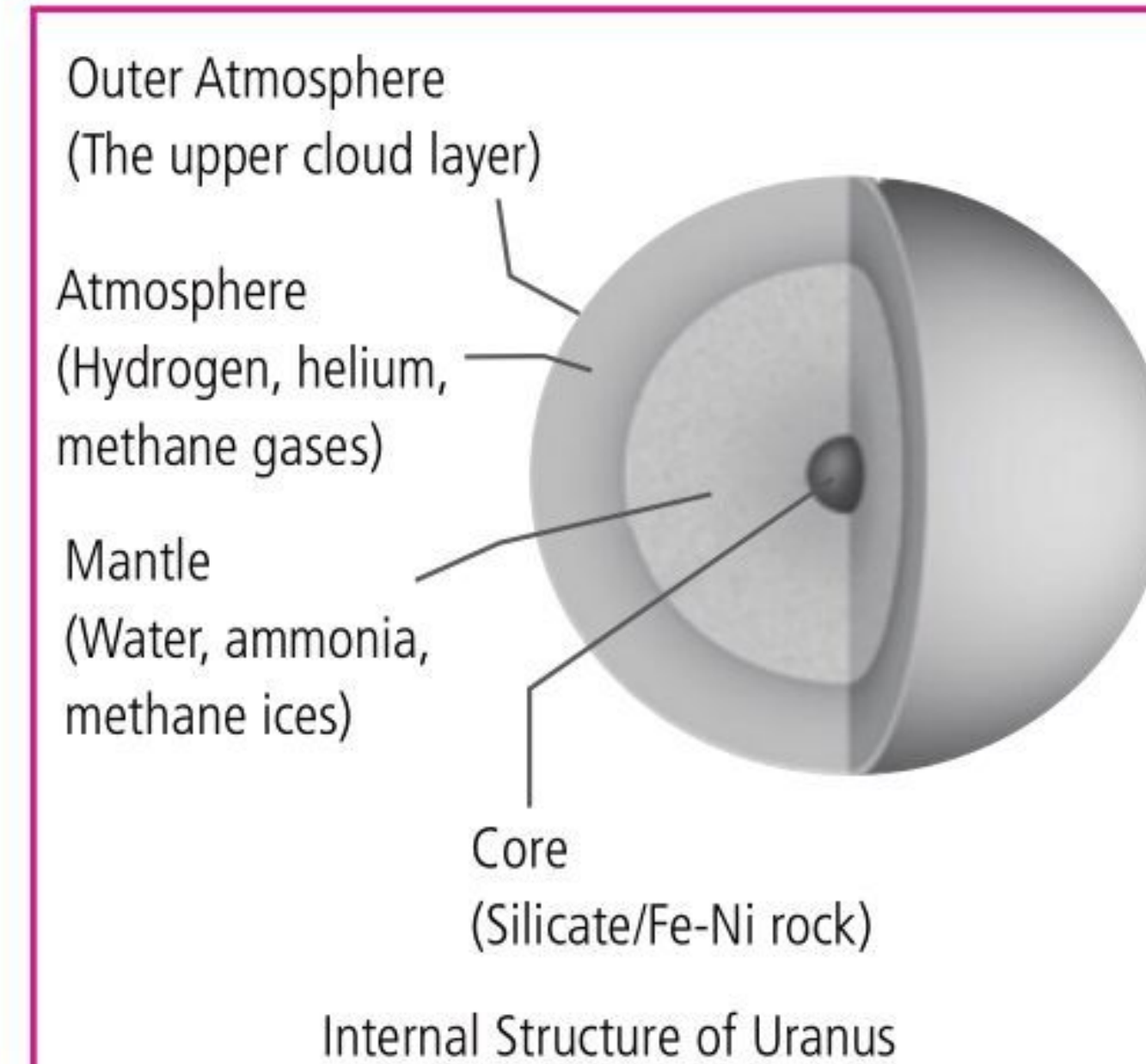
1. How Long Can Gold Wires Go?

Gold is universally used as an electricity conducting material. Its electrical conductivity is not as high as copper, but it finds many uses, since it is much more difficult to corrode (oxidise) than other metals. Besides its conducting property, gold is extremely ductile. Using metric units, one gram of gold could be drawn to a length of approximately 66 km long. It is also the most malleable of all metals, meaning it can be beaten into thinner sheets than any other metal. Gold can be beaten without any special difficulty to a thickness of 0.1 micron.



2. Why Do Coins Have a Smell?

Scientists have sniffed out the reason for the musty, "metallic" odour you smell after handling coins or touching metal objects. A new study finds that the smell of iron is, ironically, a type of human body odour, created by the breakdown of oils in skin after touching objects that contain the element. Upon contact with some metals (including iron), 1-octen-3-one is formed as a result of the decomposition of oils present in our skin. This chemical is the real reason responsible for the smell that we associate coins or metals with.



3. Why, the Planet Uranus, Rich in Methane and Hydrogen, Does not Burn?

Planet Uranus is indeed rich in extremely flammable gases, methane and hydrogen. But the burning of these gases requires oxygen. Since Uranus contains effectively zero free oxygen, hence, the hydrogen and methane in the atmosphere do not burn or explode. Interestingly, the methane in the atmosphere is what gives Uranus its distinctive blue colour. On Earth, we are so immersed in oxygen that we tend to take it for granted.

BRUSH UP *for* NEET/JEE

CLASS-XI

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

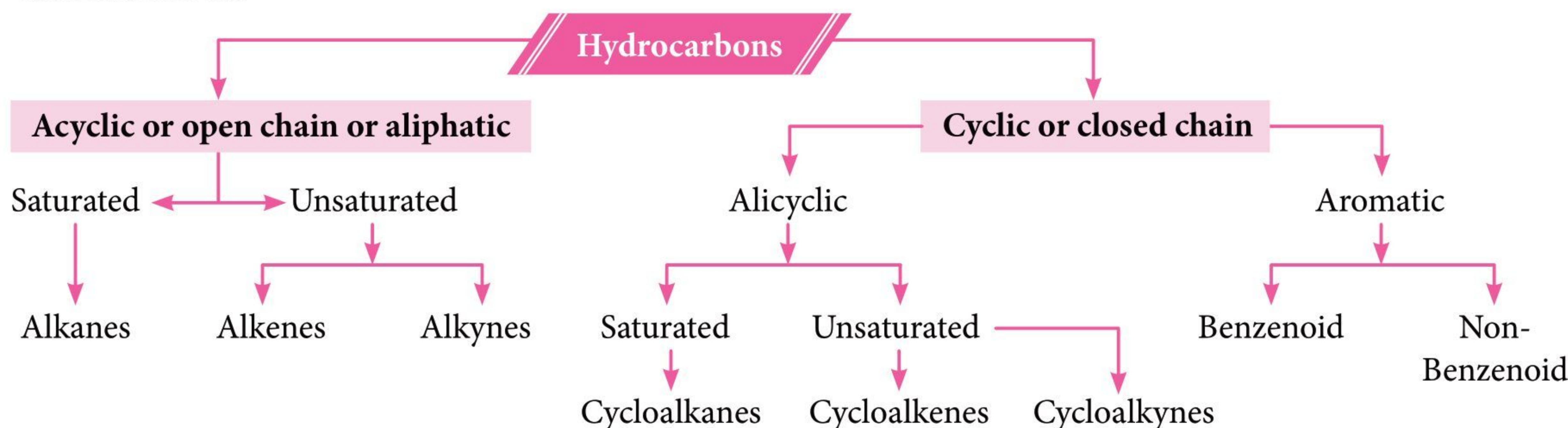
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Hydrocarbons | Environmental Chemistry

Hydrocarbons

- Organic compounds composed of only carbon and hydrogen are called *hydrocarbons*.

Classification



ALKANES

- General formula : C_nH_{2n+2} (where, $n = 1, 2, 3, 4 \dots$ etc.). Due to inertness, they are known as paraffins and only C—C and C—H single bonds are present in alkanes.

Nomenclature

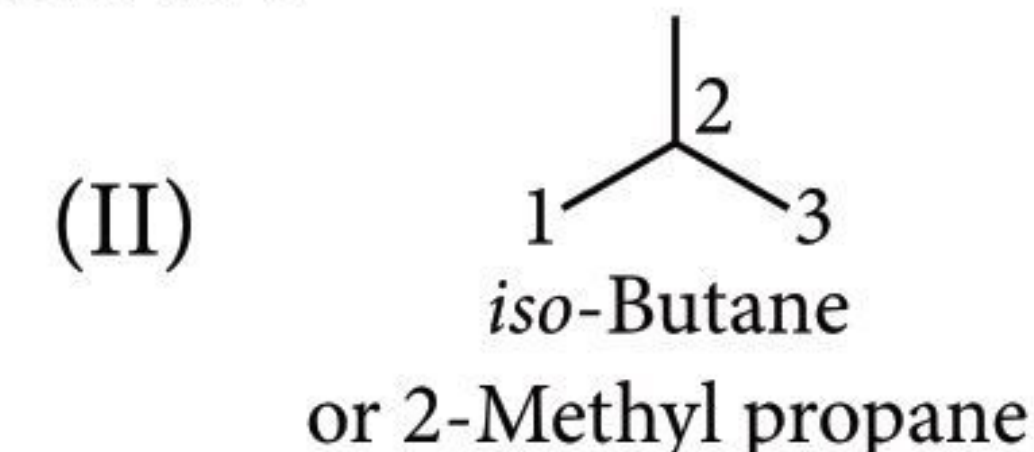
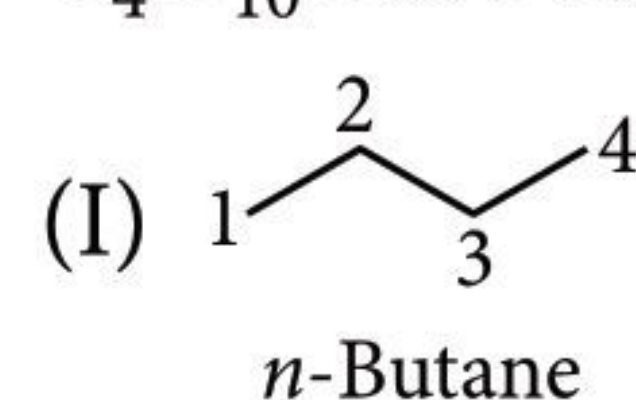
- The IUPAC names of alkanes are obtained by adding the suffix *ane* to the root word indicating the number of carbon atoms.
e.g., $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_2CH_2CH_2CH_3$
n-Butane *n*-Hexane

Isomerism

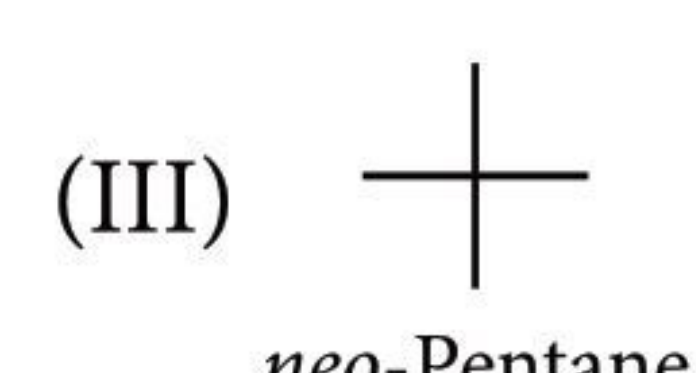
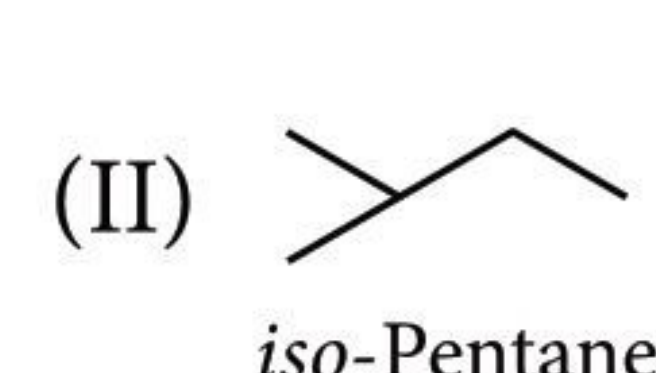
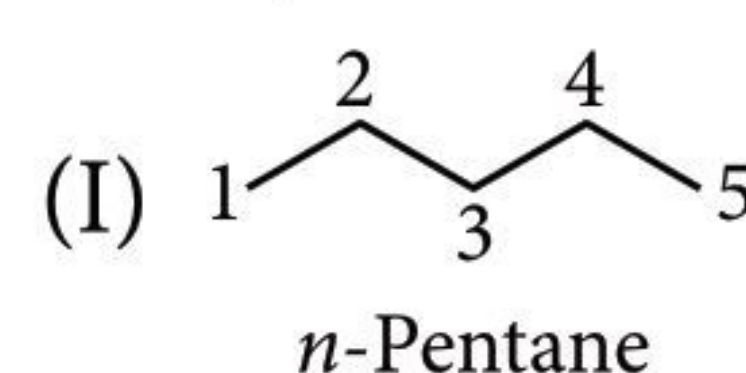
- Alkanes exhibit mainly structural (chain) isomerism and conformational isomerism.

- Structural isomerism** : Methane, ethane and propane do not exhibit isomerism.

C_4H_{10} have two chain isomers as :



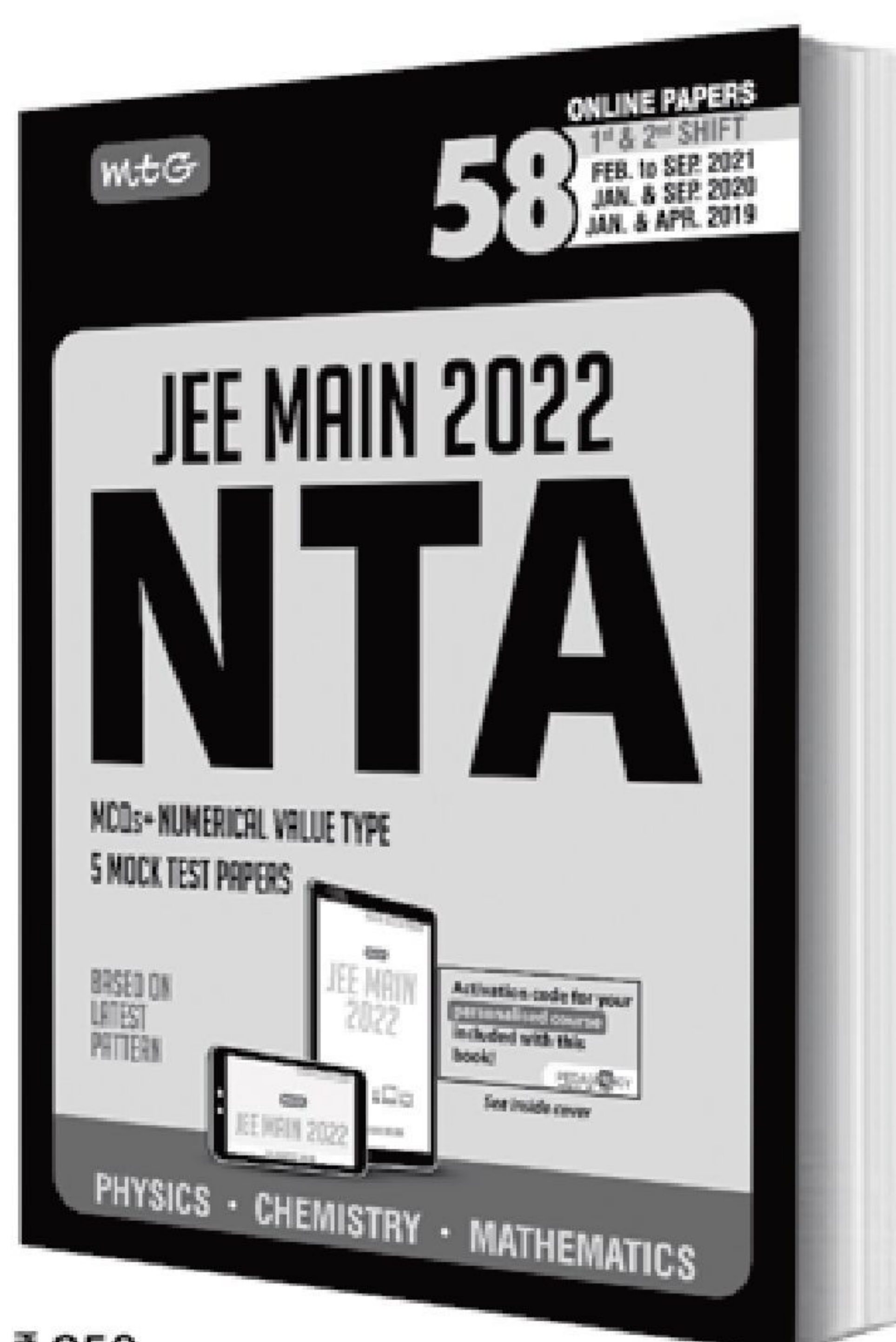
C_5H_{12} have three chain isomers as :



Conformations of Ethane (Sawhorse and Newman Projections)

- Staggered Conformation** : The hydrogen atoms attached to two carbons are far apart and experience minimum repulsion.

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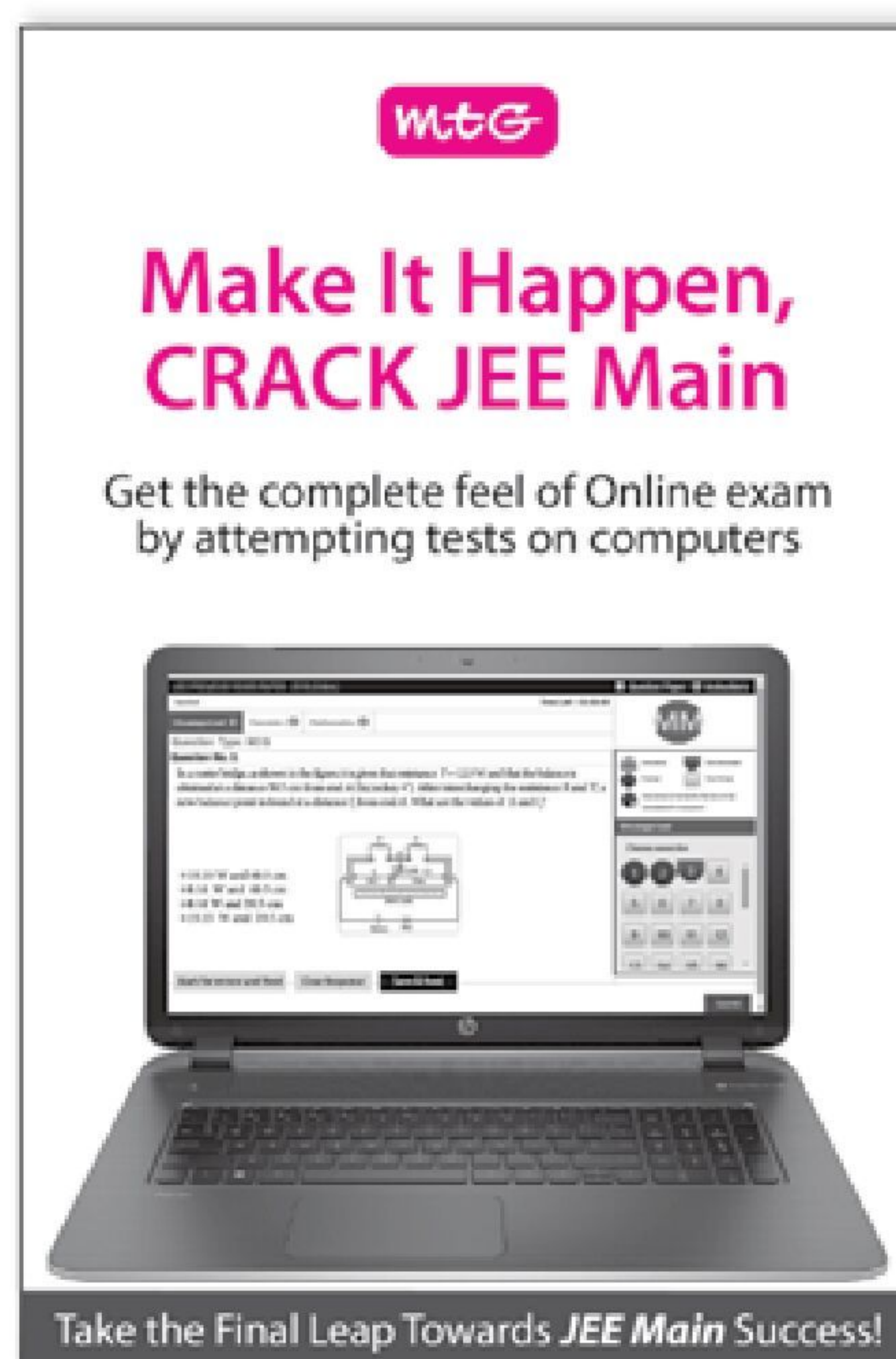
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Highlights

- Fully Solved Authentic Papers
- 26 (Feb, March, July & Sept. 2021) + 16 (Jan. & Sept., 2020) + 16 (Jan. & Apr., 2019) Online Papers
- 4915 MCQs for Practice
- Chapterwise Tabular and Graphical Analysis Showing the Weightage of Chapters
- 5 MTPs as per the latest JEE Main pattern

Practice Online Tests to Predict Your Rank

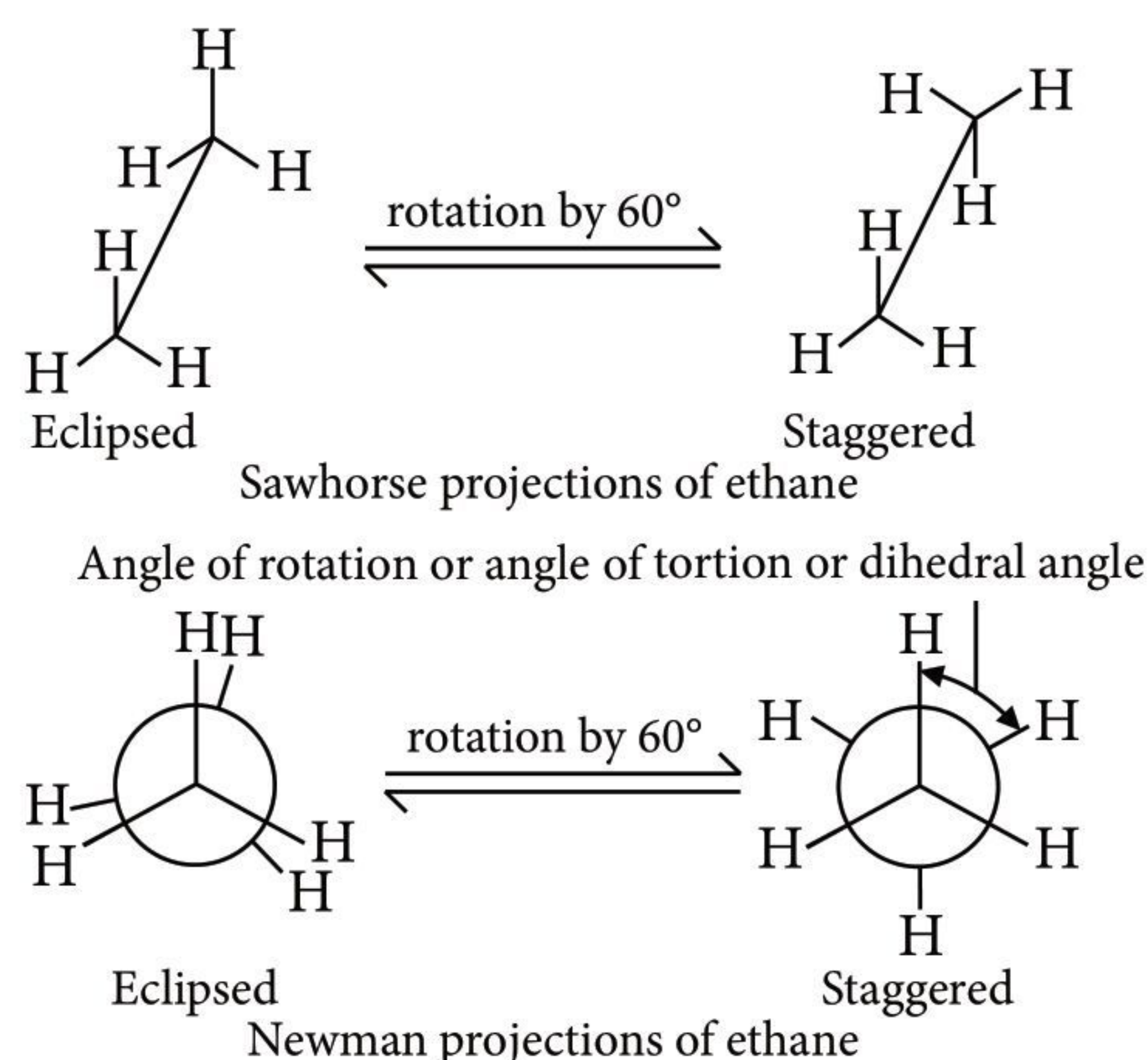
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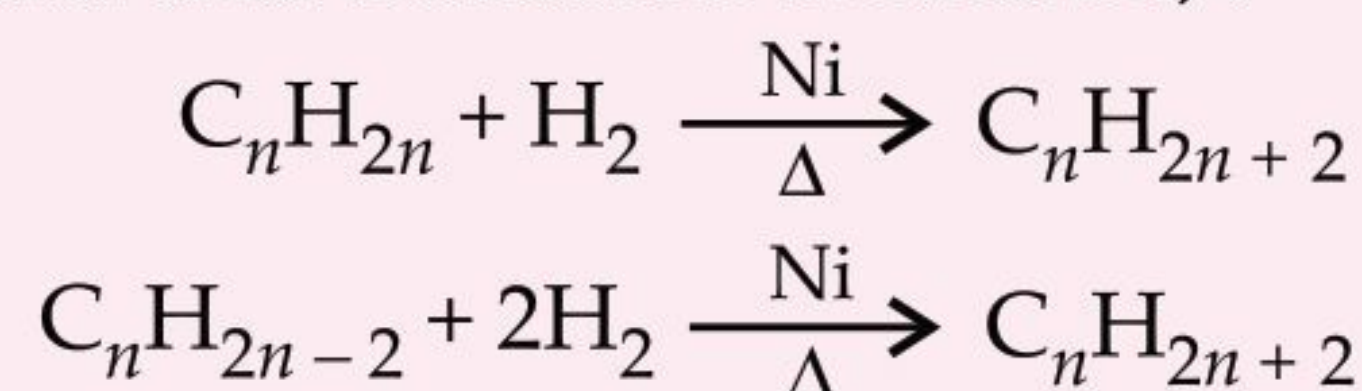


Preparation and Chemical Properties of Alkanes

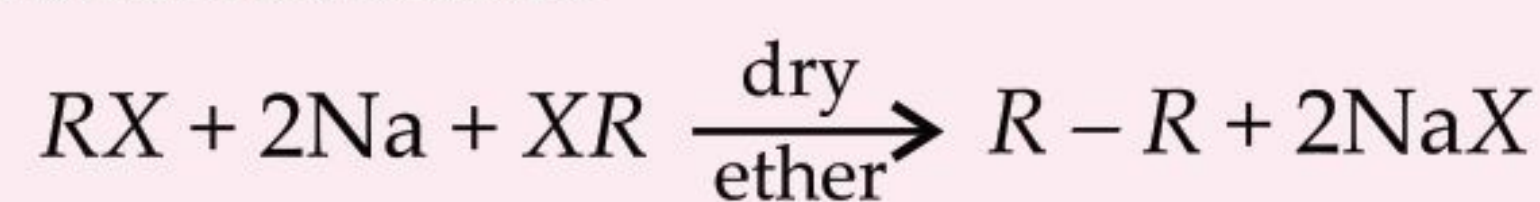
Methods of Preparation

1. By hydrogenation of unsaturated hydrocarbons

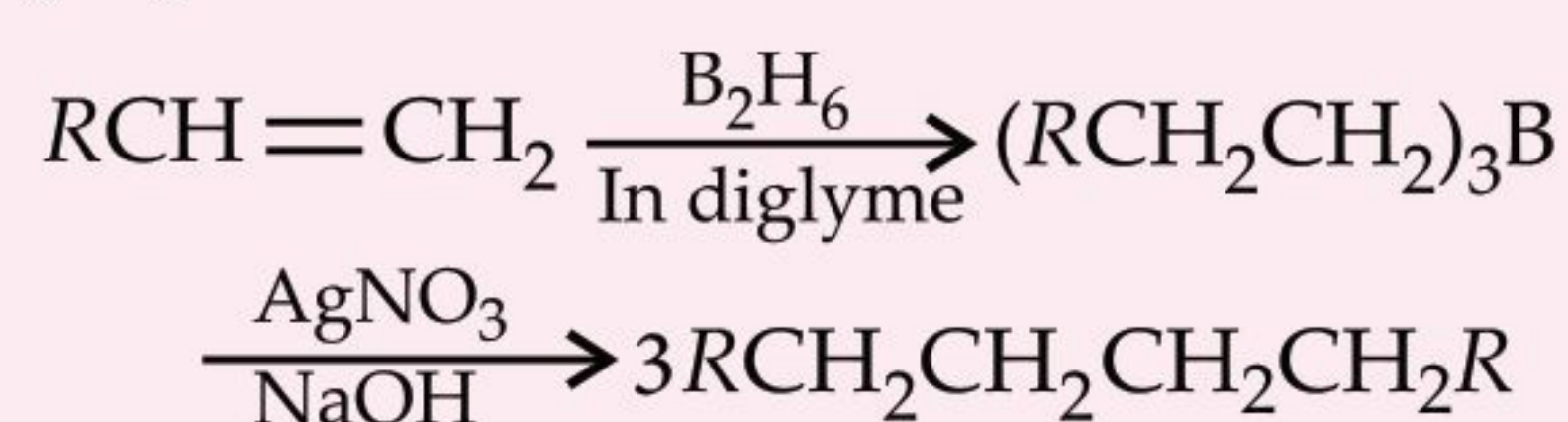
(Sabatier and Senderen's reaction):



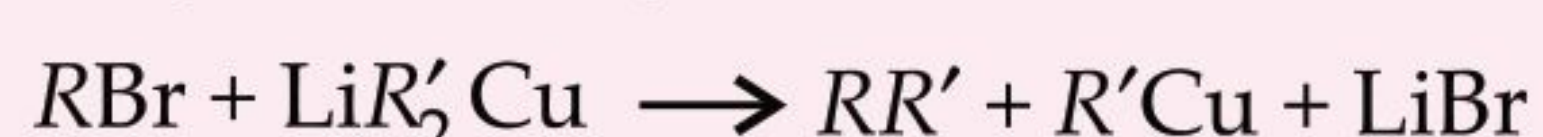
- ## 2. Wurtz reaction :



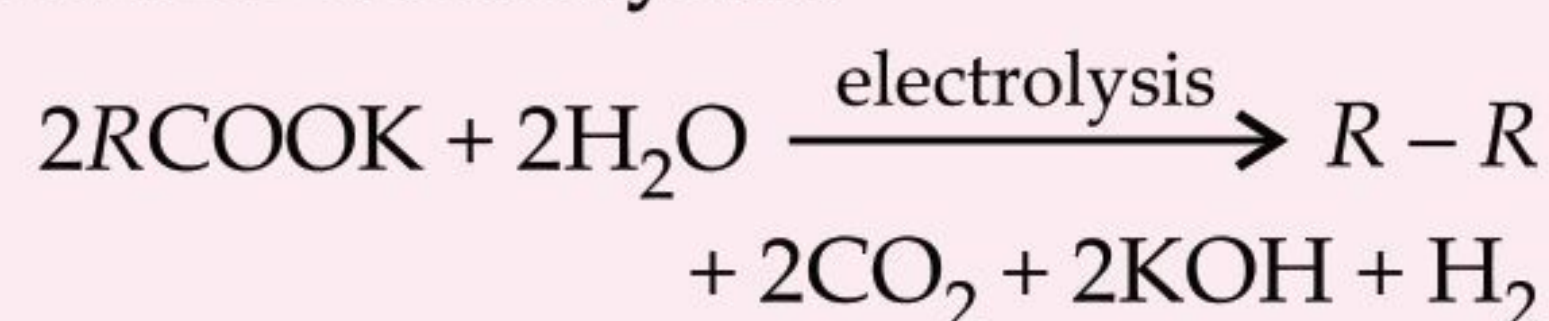
- ### 3. By hydroboration of alkenes :



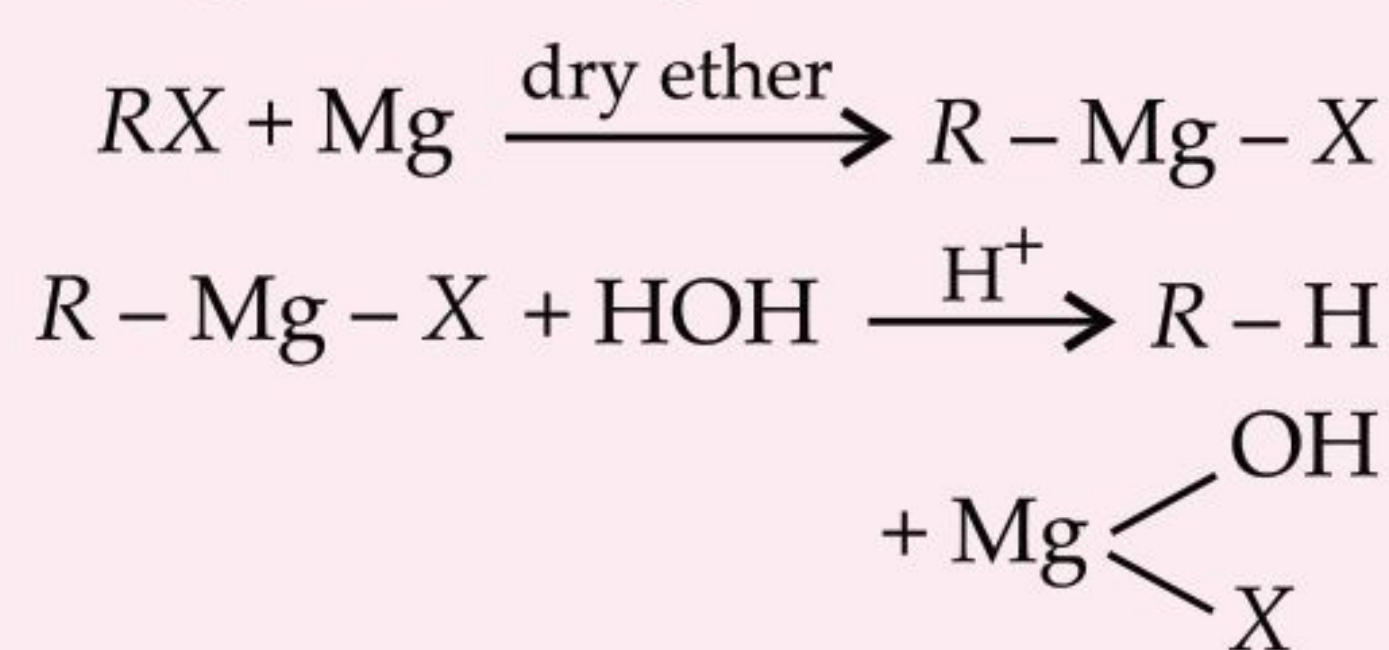
- #### 4. Corey–House synthesis :



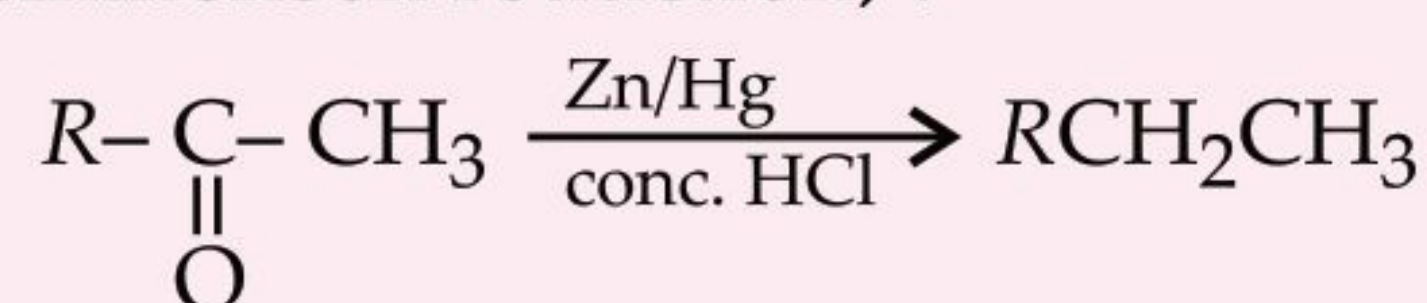
- ### 5. Kolbe's electrolysis :



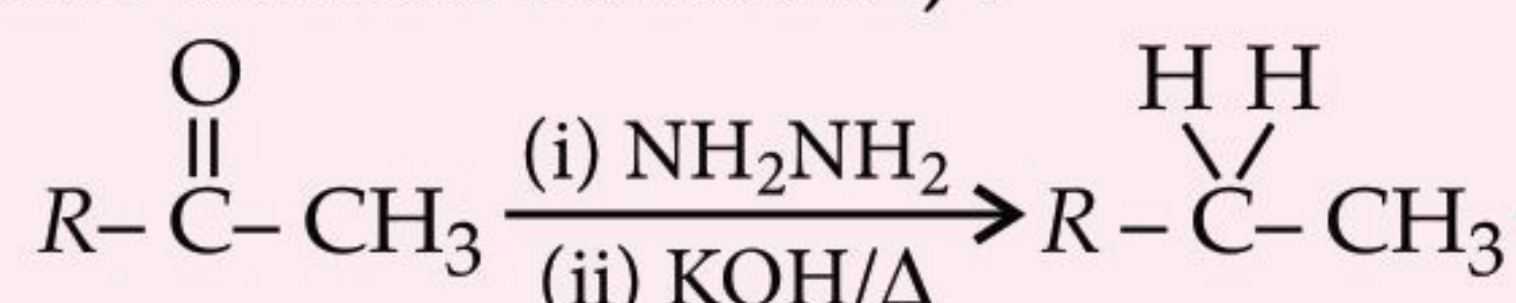
- ### 6. From Grignard's reagent :



- ### 7. From carbonyl compounds (Clemmensen reduction) :

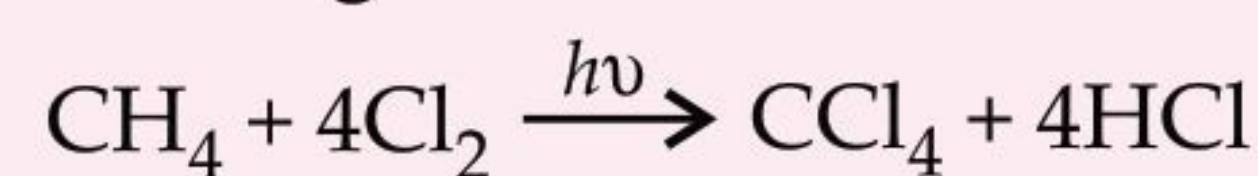


- (Wolff-Kishner reduction) :**

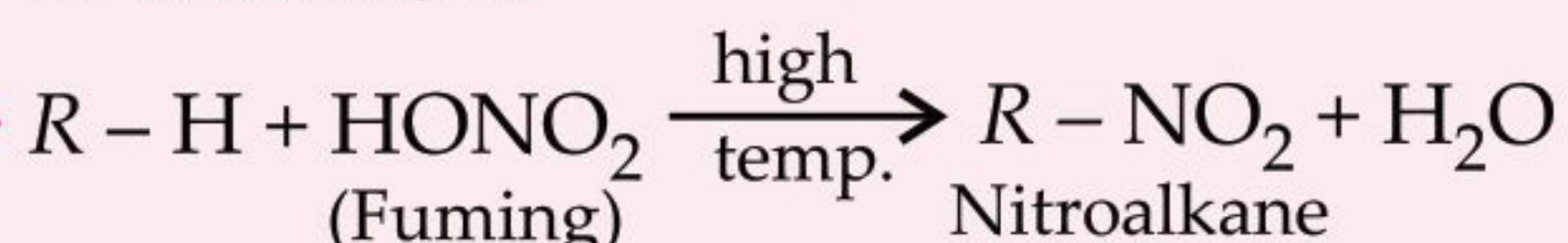


Chemical Properties

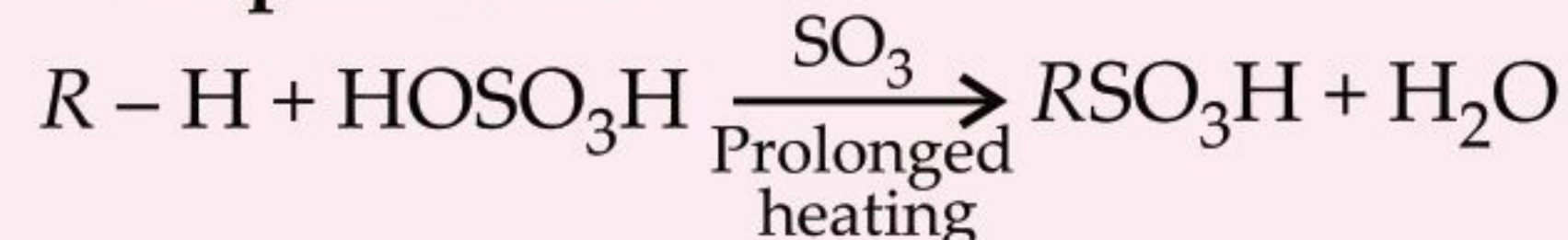
- ## 1. Halogenation :



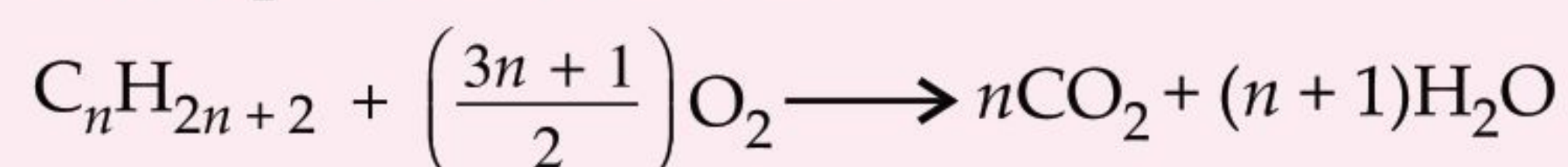
- ## 2. Nitration :



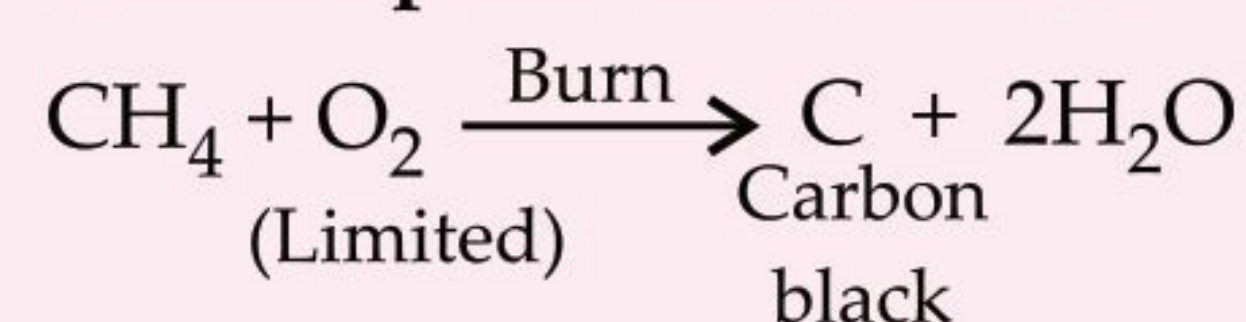
- ### 3. Sulphonation:



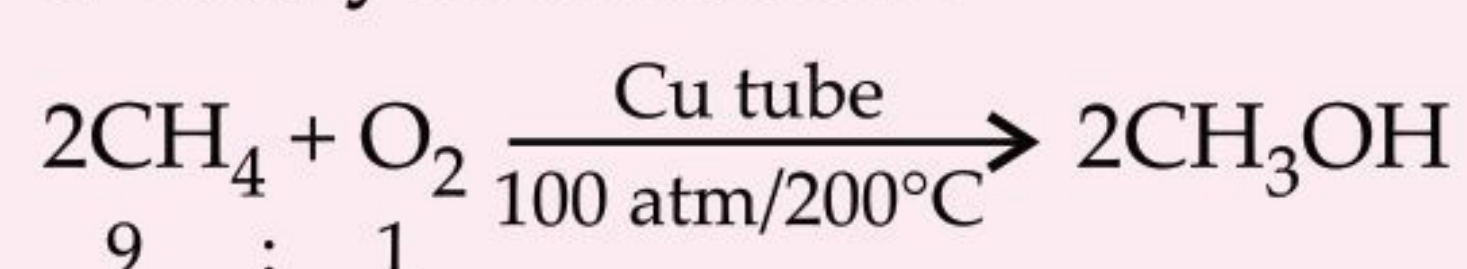
- #### 4. Complete combustion :



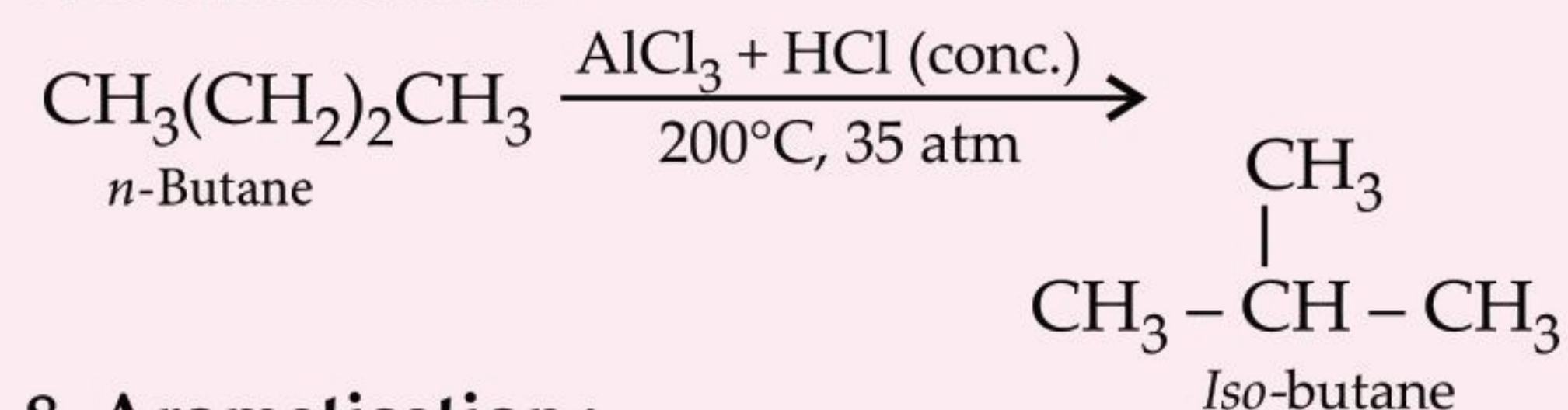
- ### 5. Incomplete combustion:



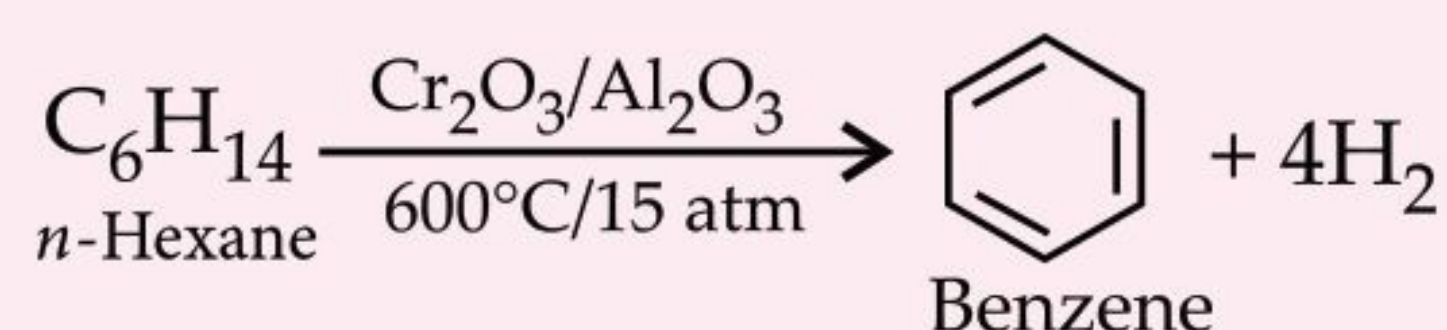
- ## 6. Catalytic oxidation:



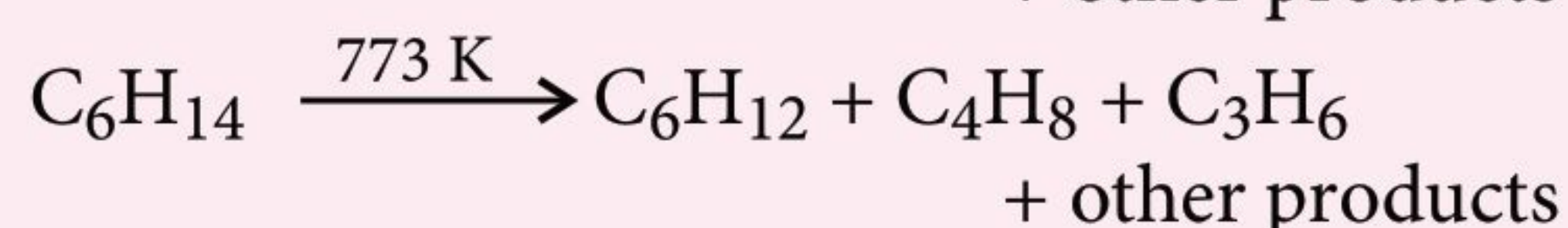
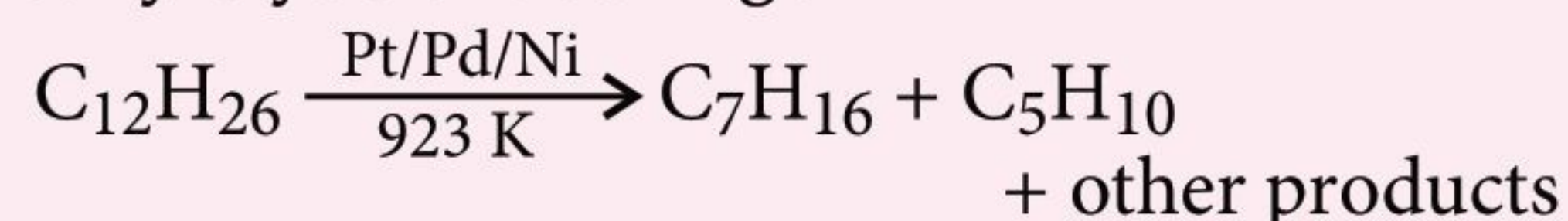
- ## 7. Isomerisation:



- ## 8. Aromatisation :



- ### 9. Pyrolysis or cracking :



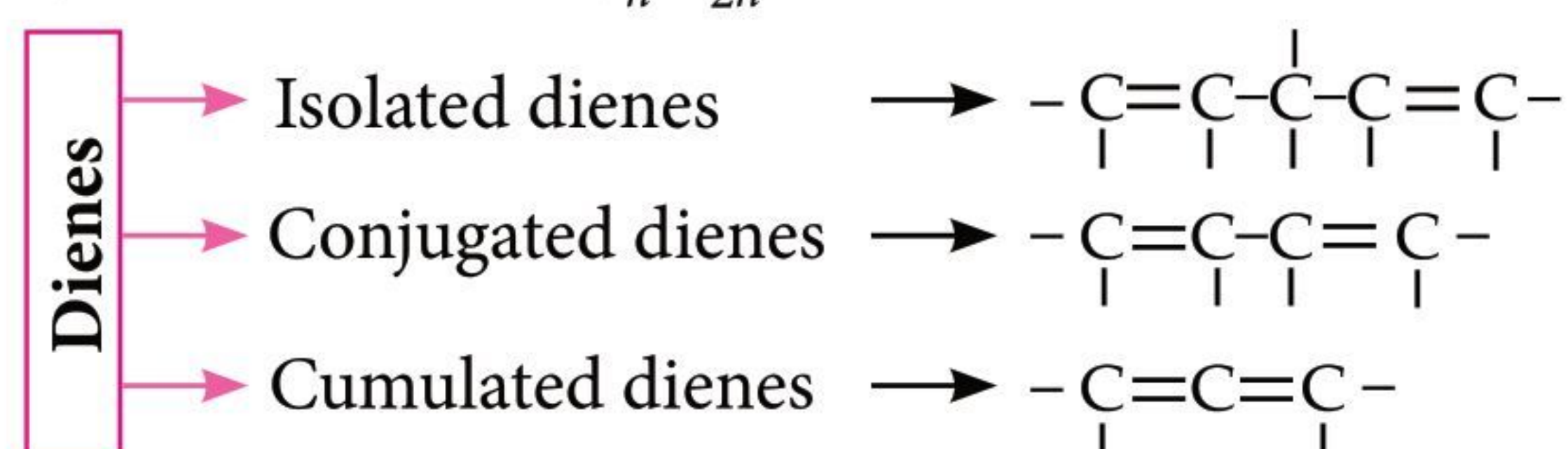
Physical Properties of Alkanes

- **Physical state** : Due to weak intermolecular forces, alkanes from C_1 to C_4 are colourless, odourless gases, C_5 to C_{17} are liquids and higher members from C_{18} onwards are waxy solids.
- **Solubility** : Alkanes are non-polar or weakly polar, hence insoluble in polar solvents like water but readily soluble in non-polar solvents like benzene, ether, carbon tetrachloride, etc. Solubility decreases with increase in molecular mass.
- **Boiling point** : Boiling points of alkanes increase regularly with increasing molecular mass. Straight chain hydrocarbons have higher boiling points than their corresponding isomeric alkanes because surface area of branched chain alkanes (isomeric alkanes) is lesser than that of straight chain alkanes, by virtue of which they experience lower magnitude of van der Waals' forces.
- **Melting point** : Melting points of alkanes also increase with the increase in molecular weight but the increase is not so regular.
- **Density** : The relative densities of alkanes increase with increase in molecular mass, but very slowly till it becomes constant at about 0.8 g cm^{-3} .
- **Viscosity** : Viscosity of alkanes (in liquid state) increases with chain length.

ALKENES

- Organic compounds containing $C = C$ are known as *alkenes*. Alkenes with two double bonds are known as *dienes*.

General formula : C_nH_{2n}



Nomenclature

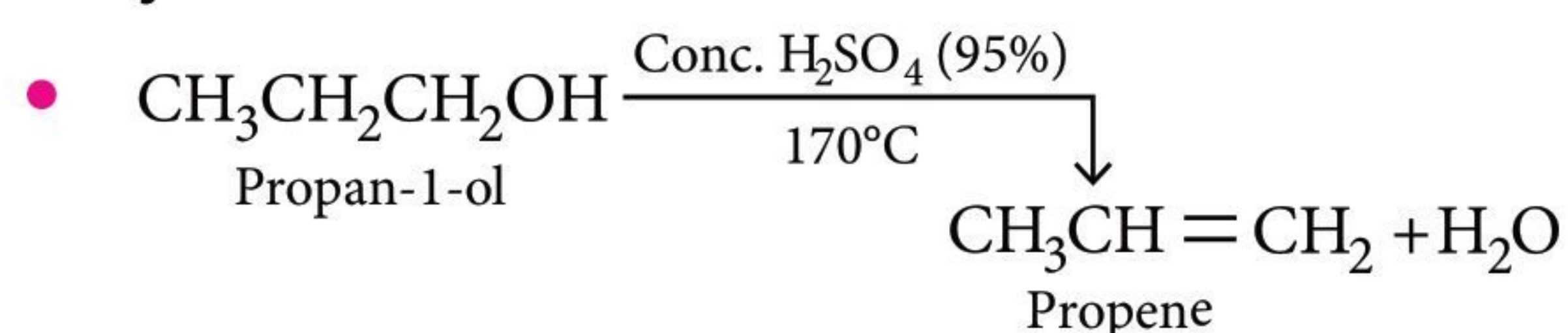
- Alkane – ane + ene = Alkene
e.g., $CH_2 = CH - CH_2 - CH_2 - CH_3$
Pent-1-ene (pentene)

Isomerism

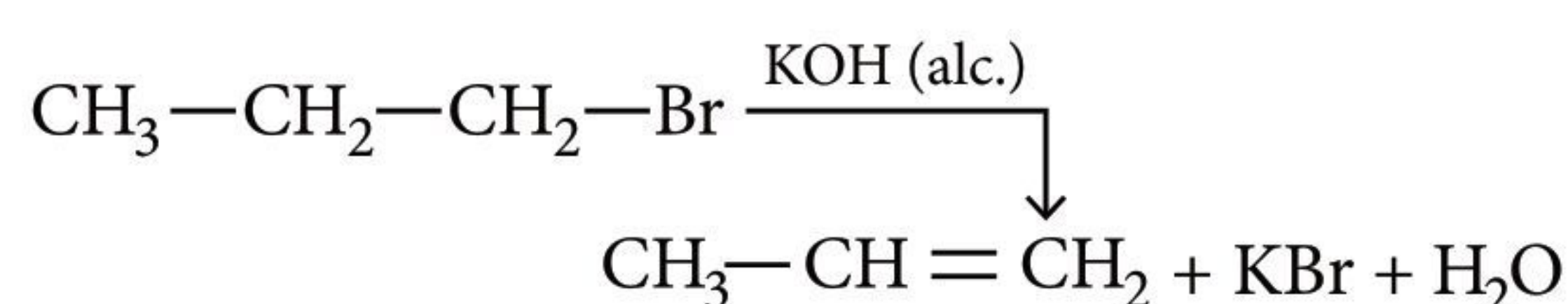
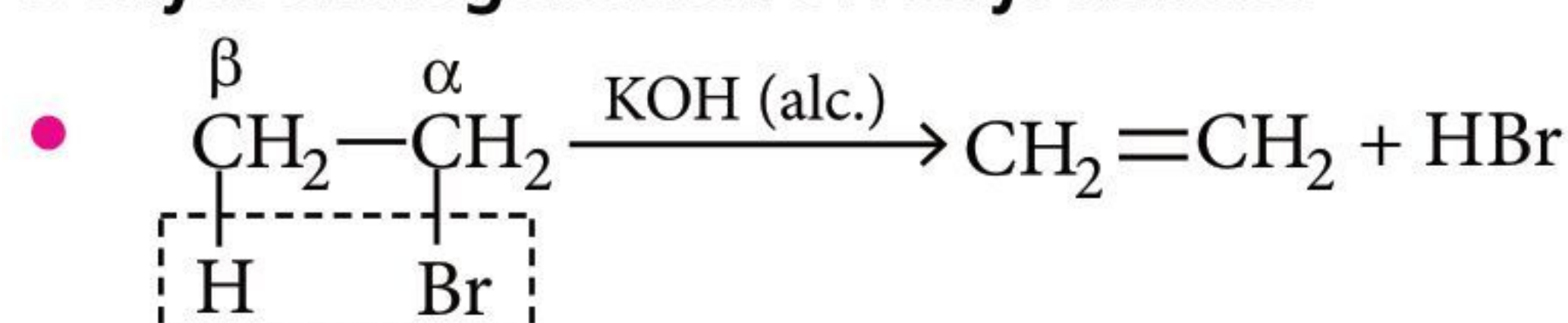
Alkenes show four types of isomerism viz., (a) Chain isomerism (b) Position isomerism (c) Geometrical isomerism (d) Ring chain isomerism.

Preparation of Alkenes

Dehydration of Alcohols



Dehydrohalogenation of Alkyl Halides



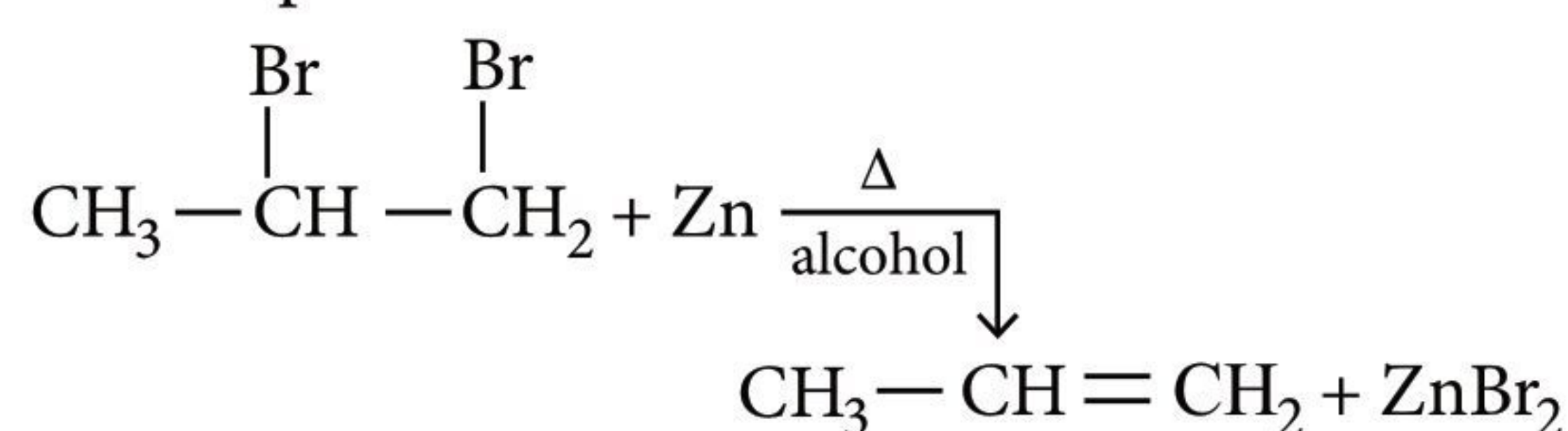
Dehydrohalogenation may proceed *via* E1 or E2 – β -elimination. The reactivity order of different alkyl halides is $3^\circ > 2^\circ > 1^\circ$ and $RI > RBr > RCl$.

If an alkyl halide can undergo dehydrohalogenation to give more than one possible product, then the relative amount of different products is governed by **Saytzeff's rule**.

Formation of less substituted alkene predominantly in an elimination reaction is referred to as **Hofmann elimination**.

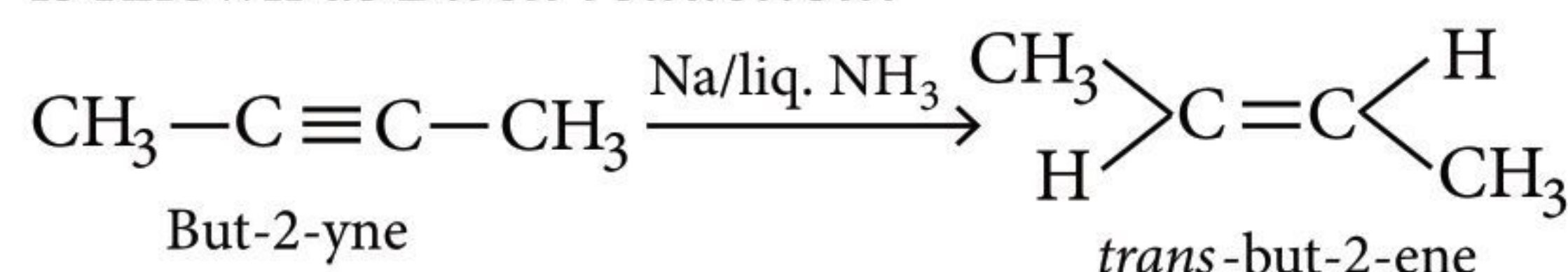
Dehalogenation of Vicinal Dihalides

- Vicinal dihalides (*i.e.*, dihalogen derivatives having halogen atoms on adjacent carbon atoms), on heating with zinc dust in methanol or NaI in acetone produce alkene.

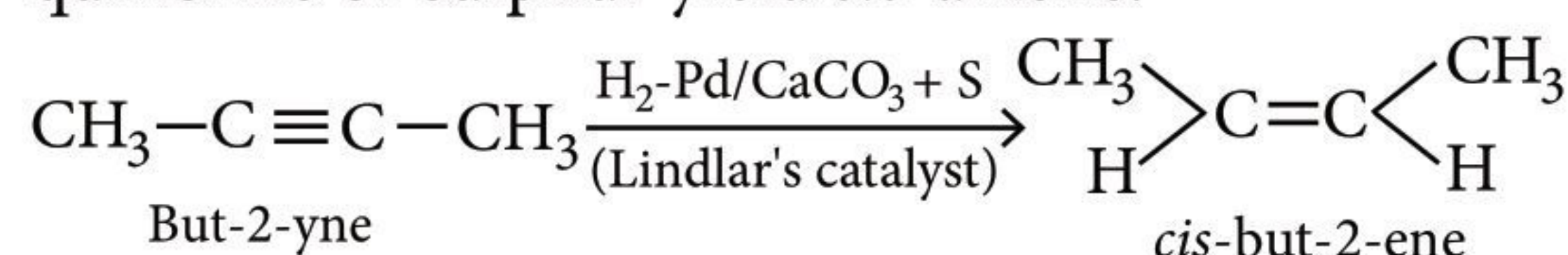


Partial Reduction of Alkyne

- Reduction of alkynes with sodium or lithium in liquid ammonia yields *trans*-alkenes. The reaction is known as **Birch reduction**.

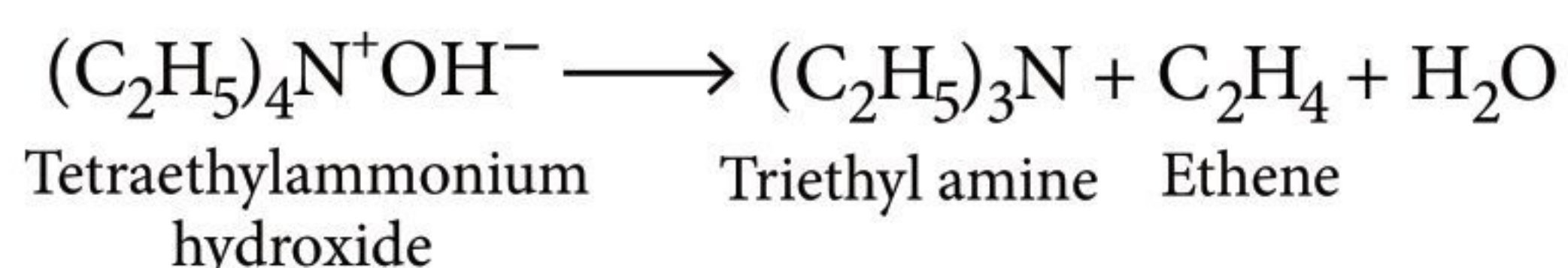


- Catalytic reduction of alkynes in presence of **Lindlar's catalyst**, *i.e.*, palladium supported over $CaCO_3$ or $BaSO_4$ and partially poisoned by quinoline or sulphur yield *cis*-alkene.



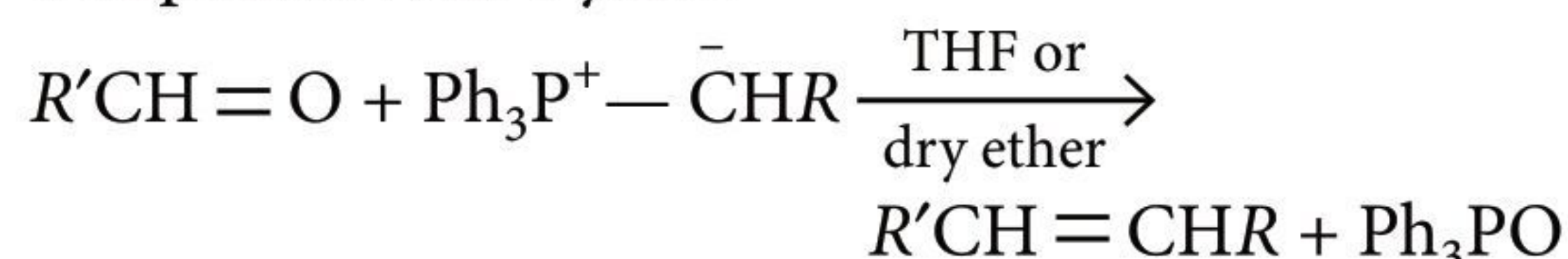
Hofmann Elimination Reaction

- Quaternary ammonium compounds on strong heating produce alkenes along with tertiary amine. The reaction involves elimination of β -hydrogen. For example,



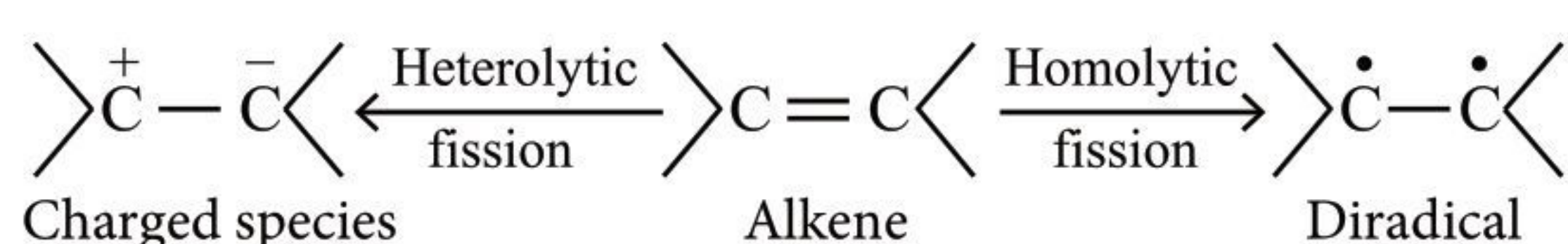
Wittig Reaction

- It is an important reaction to change a carbonyl compound into alkene by treating carbonyl compound with a ylide.

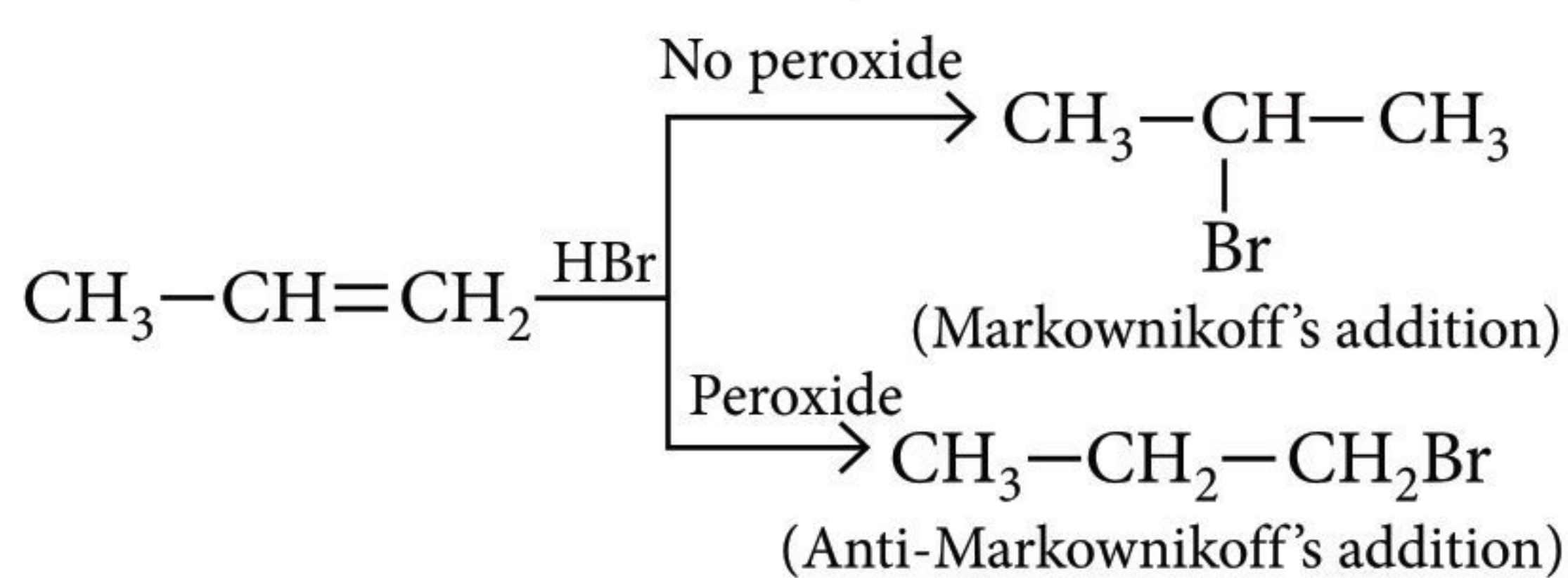
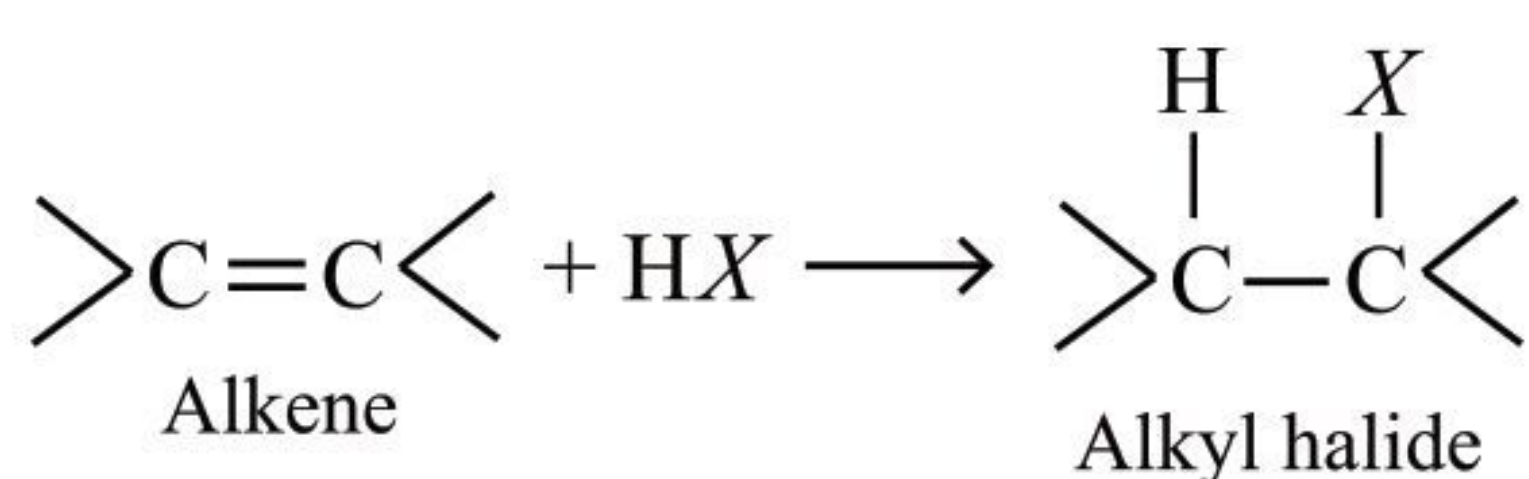


Chemical Properties of Alkenes

- The most important reactions of alkenes are the addition reactions. Alkenes are reactive due to the presence of double bond. The π -electrons are loosely held and are, therefore, easily polarisable.

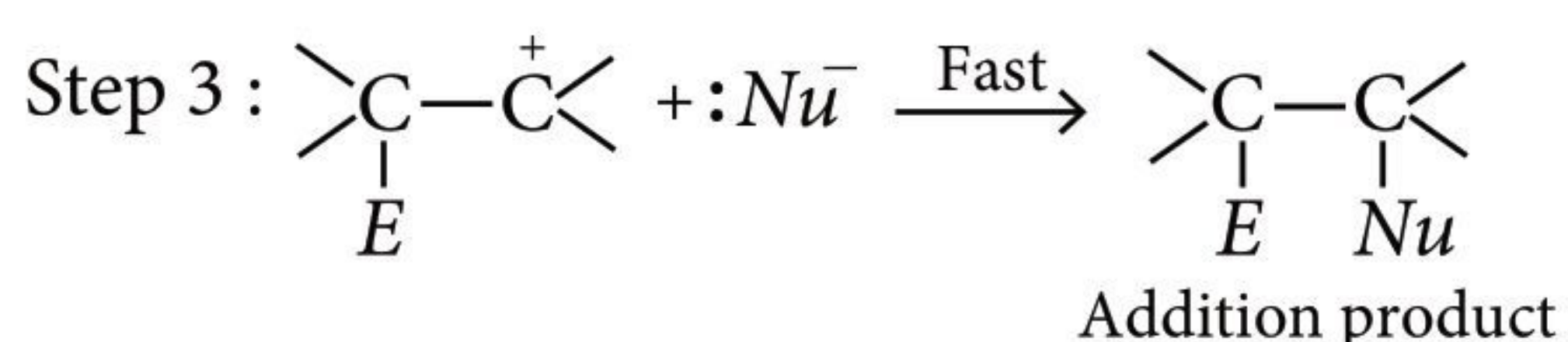
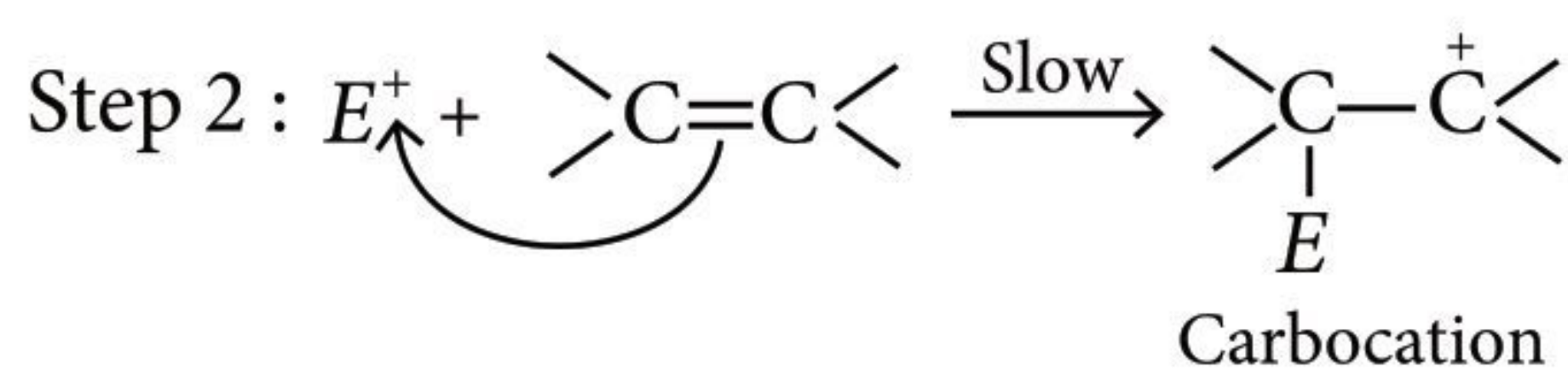
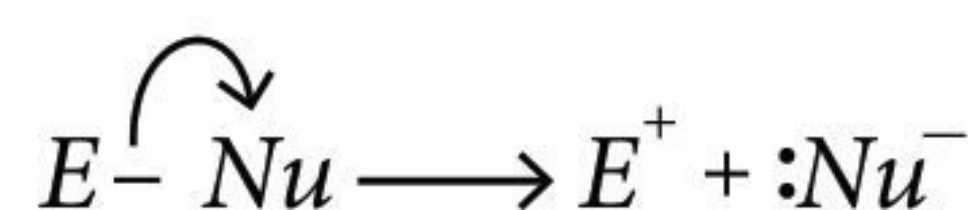


- **Addition of hydrogen halide** : Alkenes react with hydrogen halides or halogen acids to give corresponding alkyl halides.

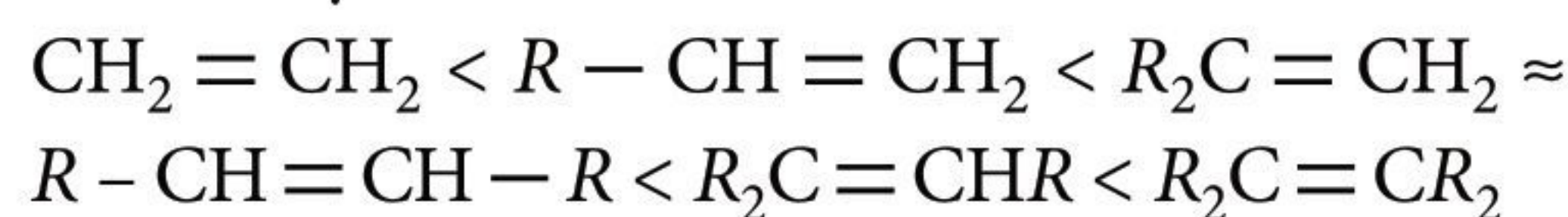


- **Mechanism of electrophilic addition :**

Step 1 : The reagent ionises

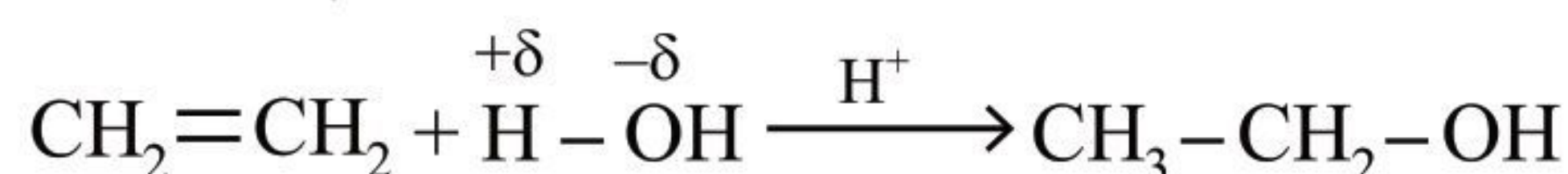


- Reactivity order :

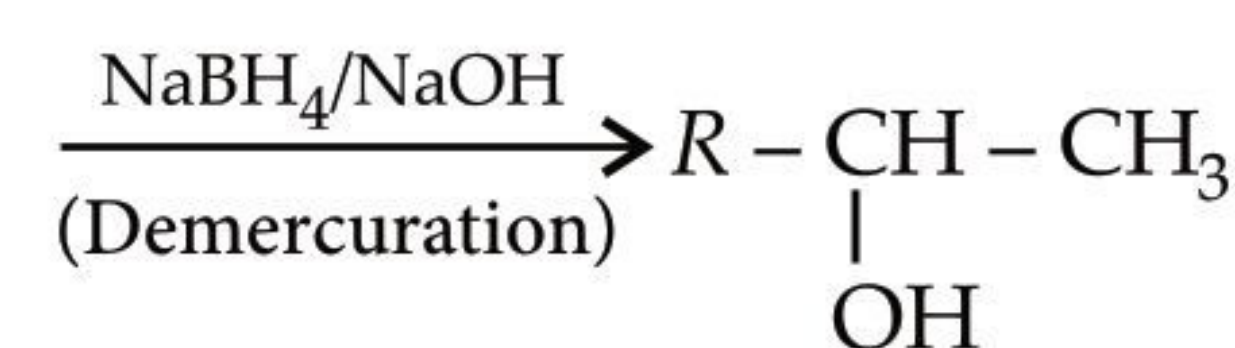
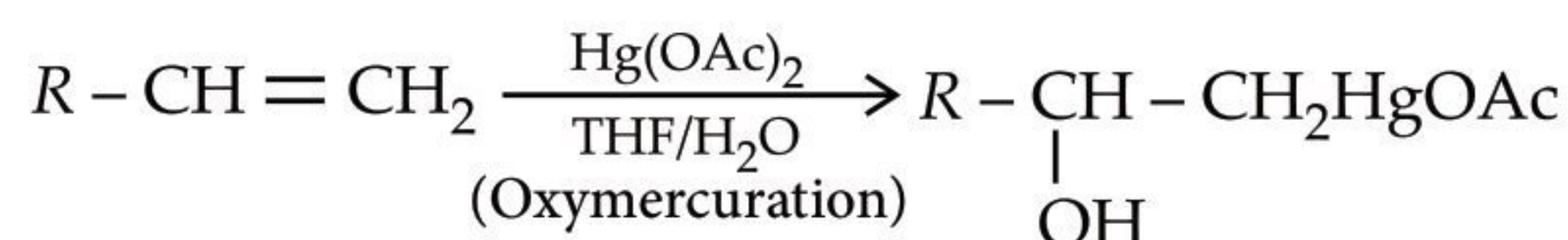


- **Addition of water :**

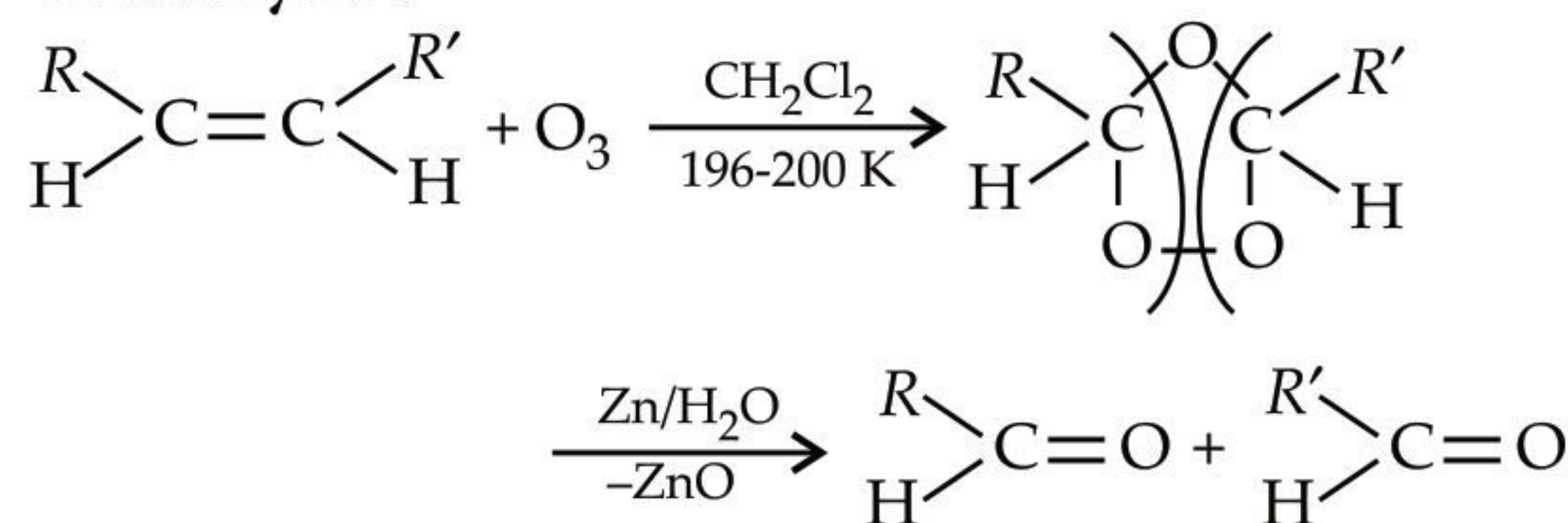
- Direct hydration of alkenes :



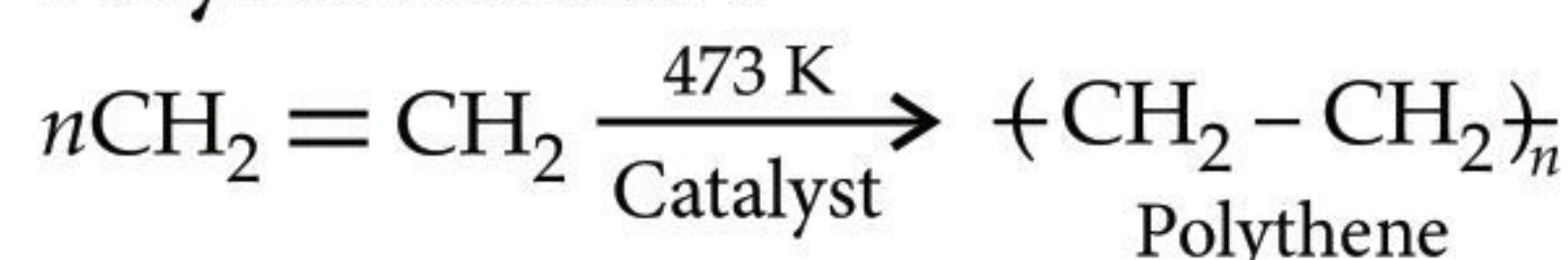
- **Oxymercuration-demercuration :**



- **Ozonolysis :**



- **Polymerisation :**



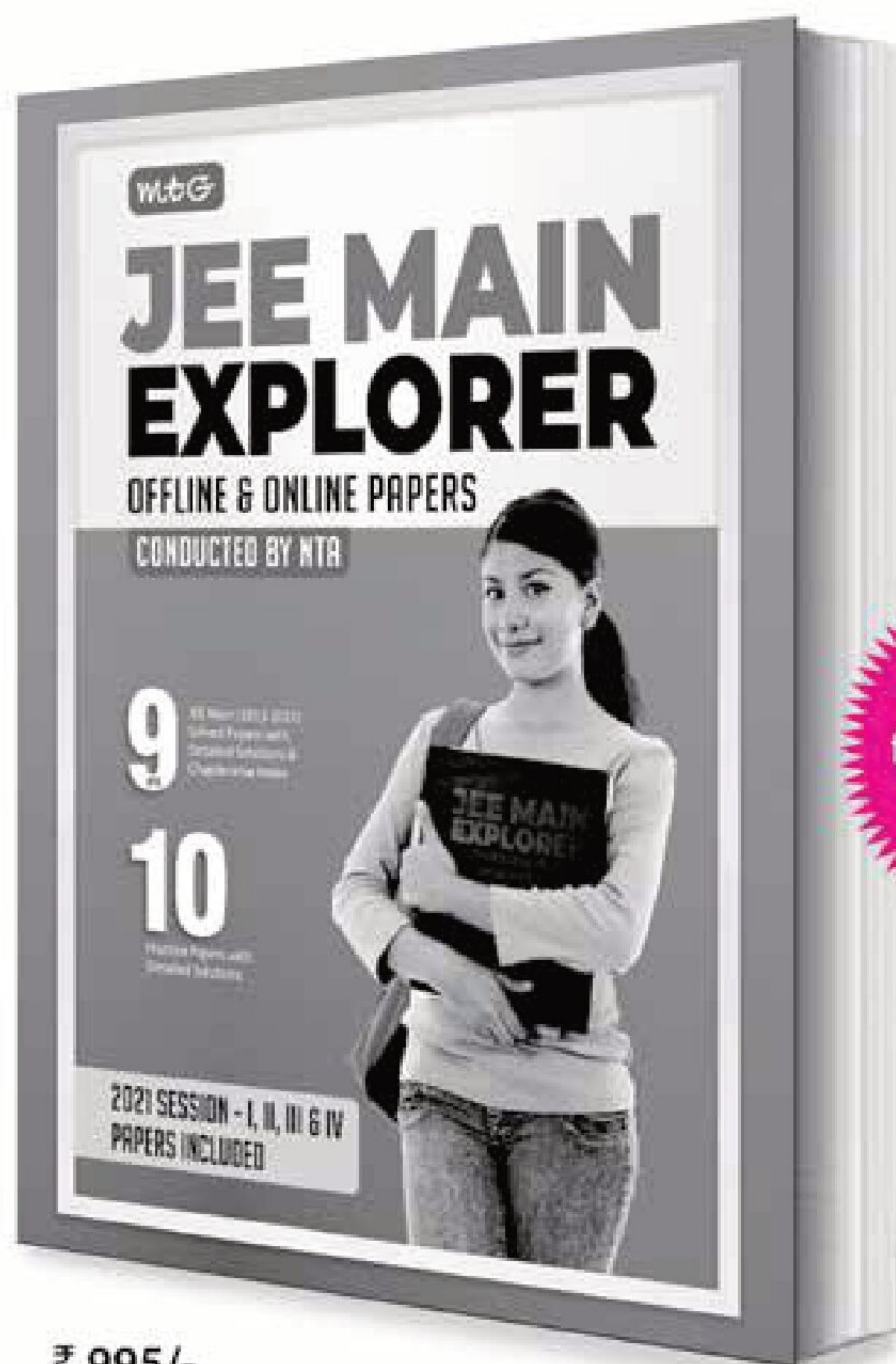
Physical Properties of Alkenes

Alkenes resemble alkanes in most of their physical properties.

- $(C_2 - C_4)$ are colourless gases, $(C_5 - C_{18})$ are liquids and next higher members are solids at room temperature.
- Melting point increases with increase in molecular mass. More symmetrical *trans*-isomer always has higher melting point than corresponding *cis*-isomer.
- Boiling point also increases with increase in molecular mass. *cis*-Alkenes have higher boiling point than corresponding *trans*-alkenes, because of greater dipole moment of *cis*-alkenes which results in stronger intermolecular attraction. Like alkanes, branching in alkenes lowers the boiling point.
- Alkenes are insoluble in water but soluble in non-polar solvents like CCl_4 , benzene, ether, etc.
- Alkenes are lighter than water.
- Alkenes are generally non-polar but certain unsymmetrical alkenes are slightly polar. For example, propene has dipole moment of 0.35 D.



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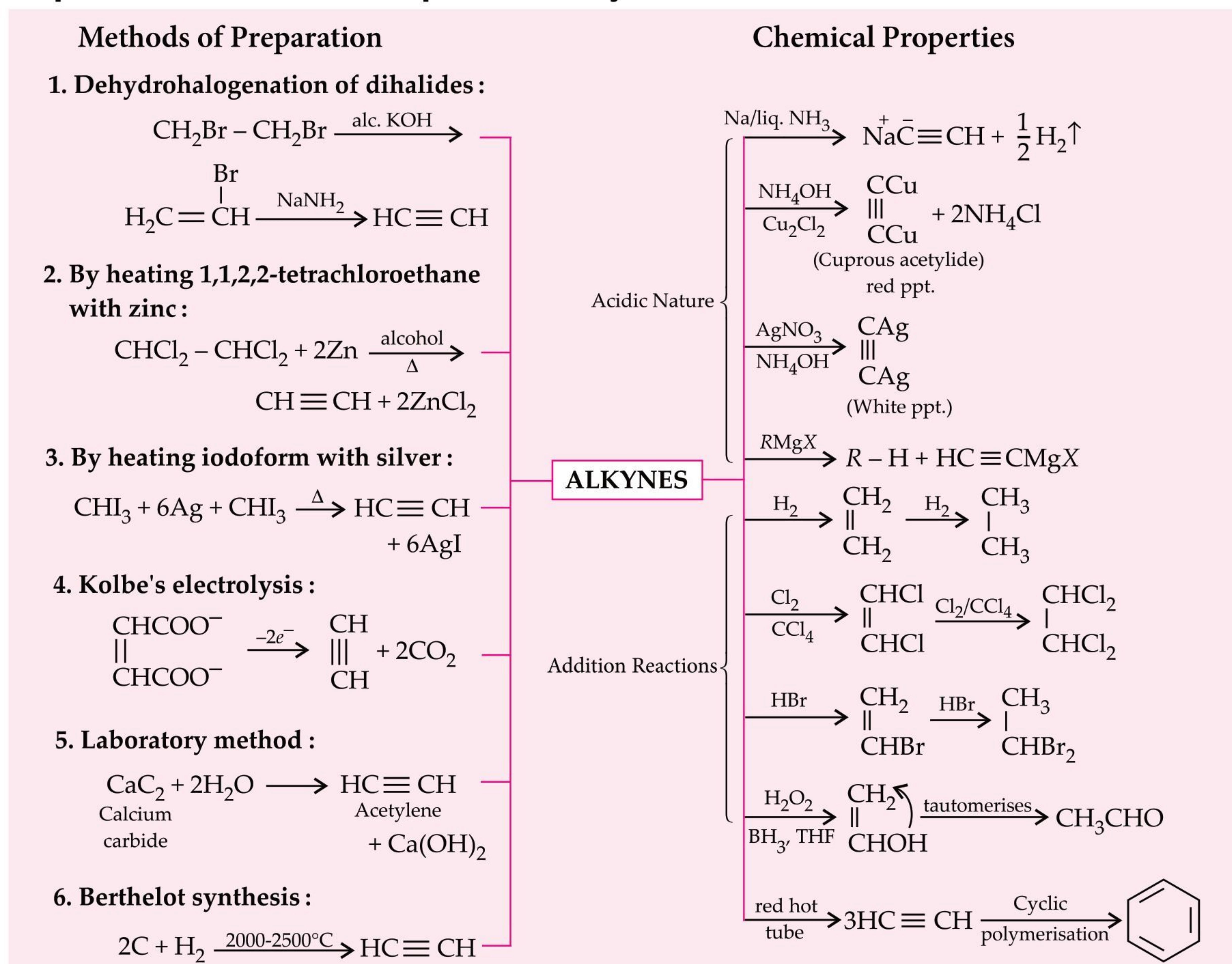
ALKYNES

- Hydrocarbons with $C \equiv C$ are known as *alkynes*.
General formula of alkynes is C_nH_{2n-2} .

Nomenclature

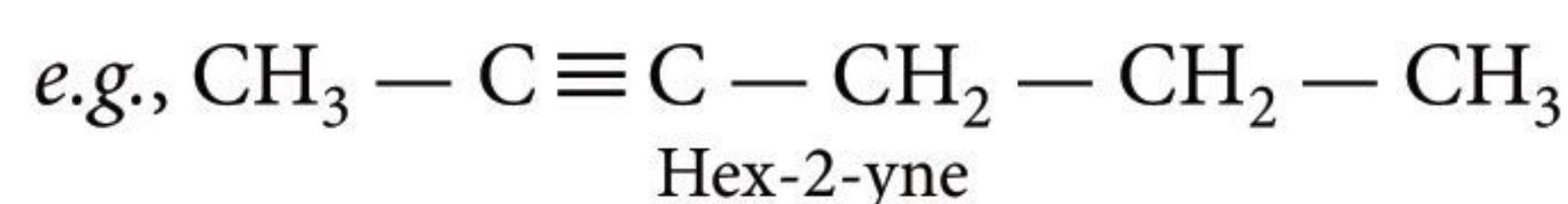
- Alkane – ane + yne = Alkynes

Preparation and Chemical Properties of Alkynes



Physical Properties of Alkynes

- Colourless and odourless with the exception of acetylene which has a characteristic odour.
- First three members are colourless gases, next eight are liquids and the higher ones are solids.
- Alkynes are slightly more polar than alkenes because of *sp*-hybridised carbon. In addition to it terminal alkynes are more polar than internal alkynes.
- Melting point and boiling point of simple alkynes are slightly higher than corresponding alkanes and



Isomerism

Ethyne does not show any type of isomerism. Higher alkynes form chain, position, functional and also metamers.

alkenes. This can be attributed to their symmetrical linear shape, so that molecules can pack more closely in the crystal lattice.

- Insoluble in water but readily soluble in non-polar solvents.
- Lighter than water.

Acidic Character of Alkynes

- Hydrogens in terminal alkynes are relatively acidic. But acetylene ($pK_a = 25$) is far weaker acid than water ($pK_a = 15.7$) or alcohols ($pK_a = 16-19$).

However, it is much more acidic than ammonia ($pK_a = 34$). In contrast to it alkanes and alkenes do not show any acidic character.

Electrons of C—H bond in acetylene are strongly held by carbon nuclei which facilitate the removal of hydrogen as proton. Thus, relative order of acidic character of various compounds can be given as : $H_2O > ROH > HC \equiv CH > NH_3 > CH_2 = CH_2 > CH_3-CH_3$.

By virtue of their acidic character, terminal alkynes form salts which are known as alkynides or acetylides.

Aromatic Hydrocarbons

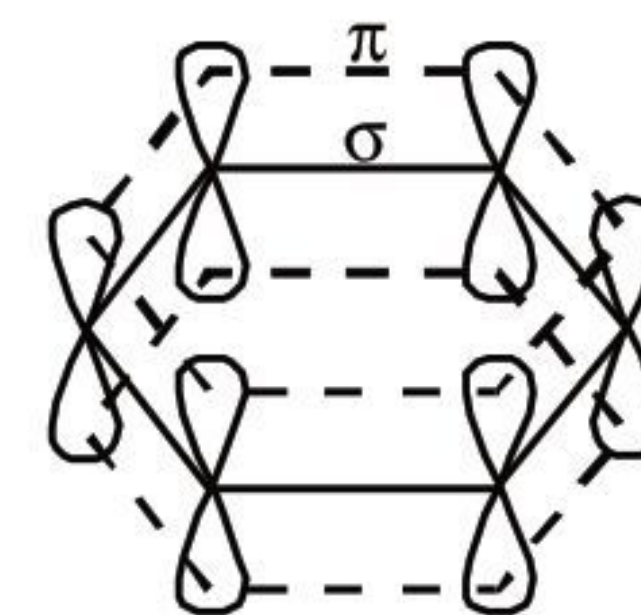
- Aromatic compounds refer to benzene and related compounds. They have a pleasant odour, hence they are termed aromatic (aroma-fragrance or smell). Aromatic hydrocarbons containing benzene ring are called benzenoids whereas those not containing a benzene ring are called non-benzenoids.

Structure of Benzene

- All six carbon atoms in benzene are sp^2 hybridised.
- The sp^2 hybrid orbitals overlap with each other and with s-orbitals of the six hydrogen atoms forming

C – C and C – H σ bonds respectively.

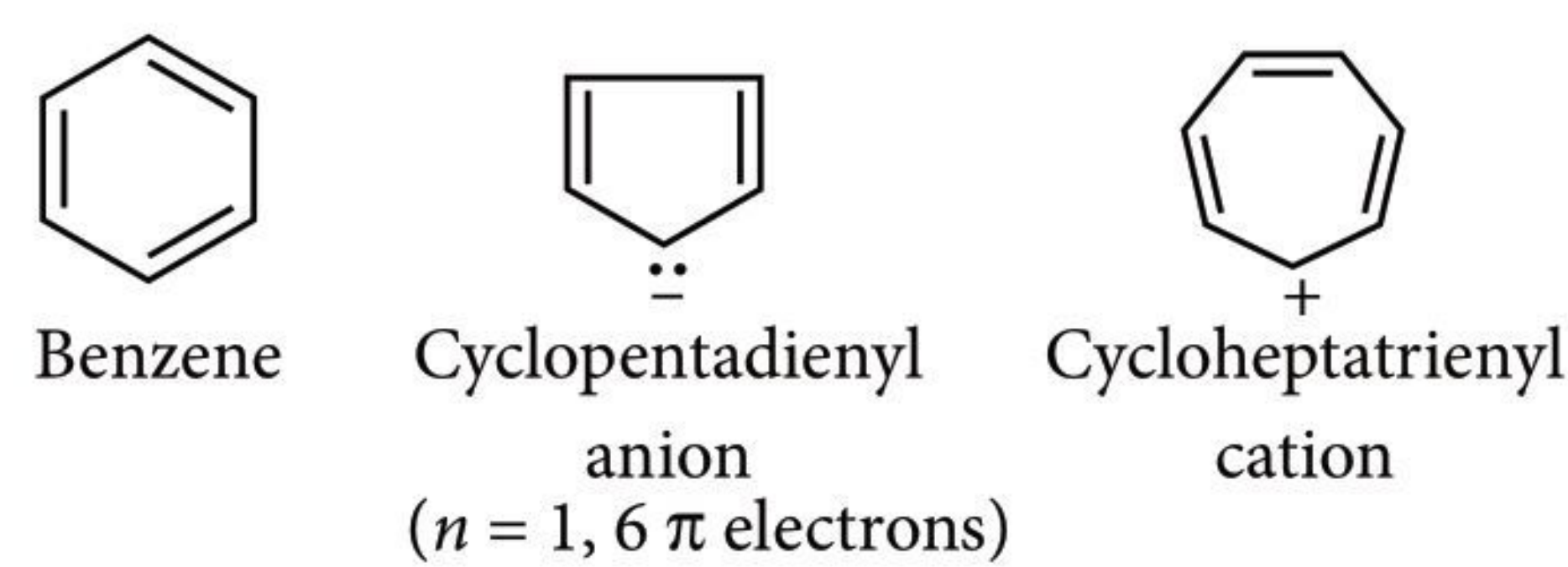
- All σ -bonds in benzene lie in one plane and all bond angles are 120° .
- One half of π -molecular orbitals lies above and the other half lies below the plane of the σ -bond.



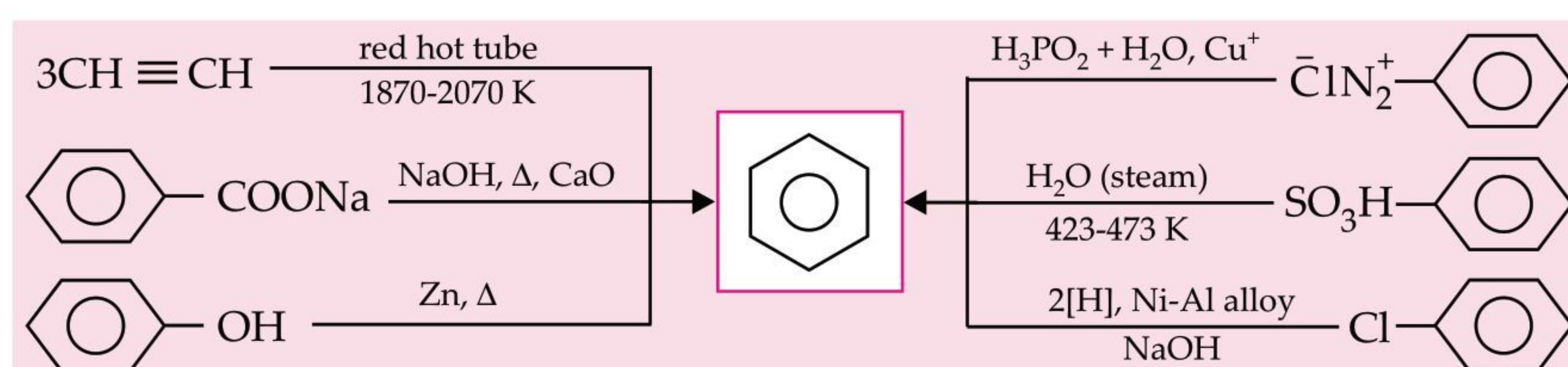
- Aromaticity (Huckel Rule) :** Huckel rule of aromaticity is applied to all the ring systems whether they have benzene ring or not and possess the following characteristics :

- Planarity
- Complete delocalisation of π -electrons in the ring.
- Presence of $(4n + 2)\pi$ -electrons in the ring where $n = 0, 1, 2, 3, \dots$

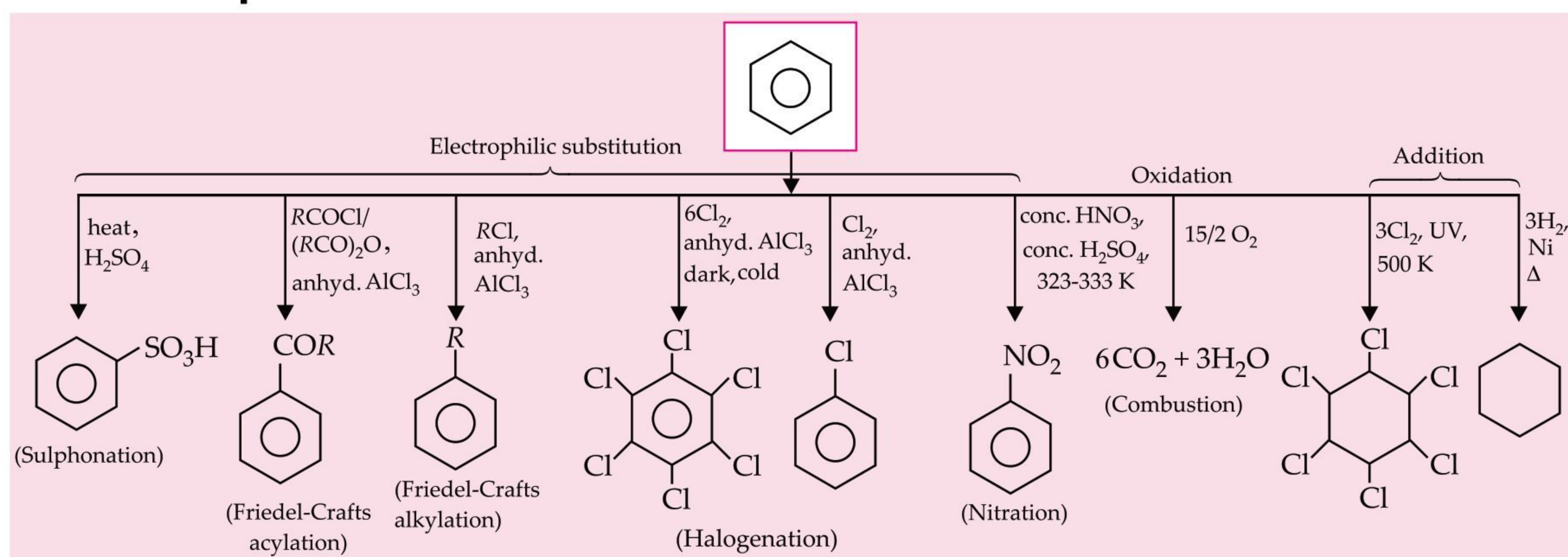
For example,



Methods of Preparation of Benzene



Chemical Properties of Benzene

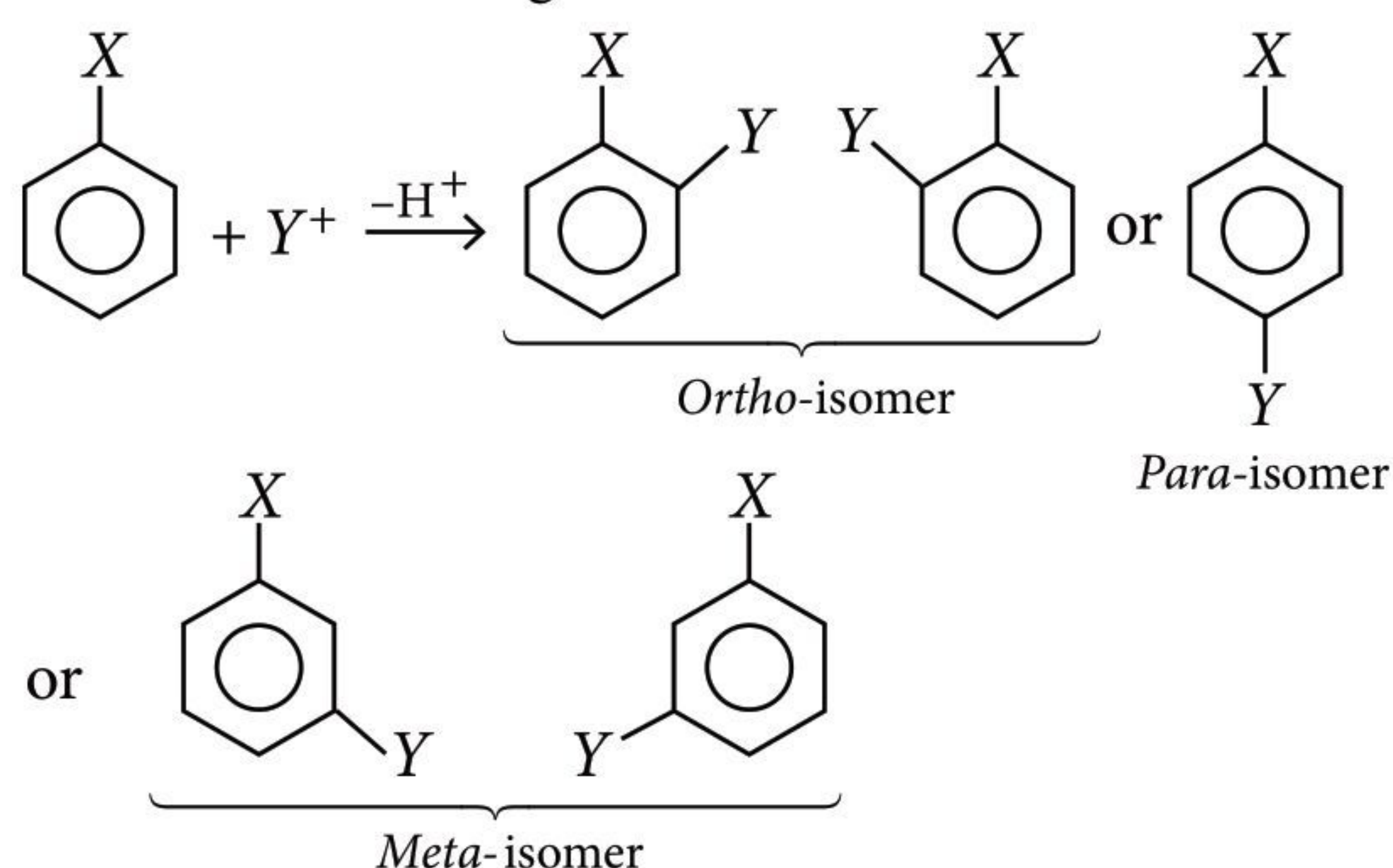


Substitution in Monosubstituted Benzene Derivatives

The substituent already present on benzene ring has directive or orientation effect as well as activity effect on further substitutions.

Directive or orientation effect

- The second substituent may enter the benzene ring at either *ortho* and *para* position or at *meta* position depending upon the nature of group already present on the benzene ring.



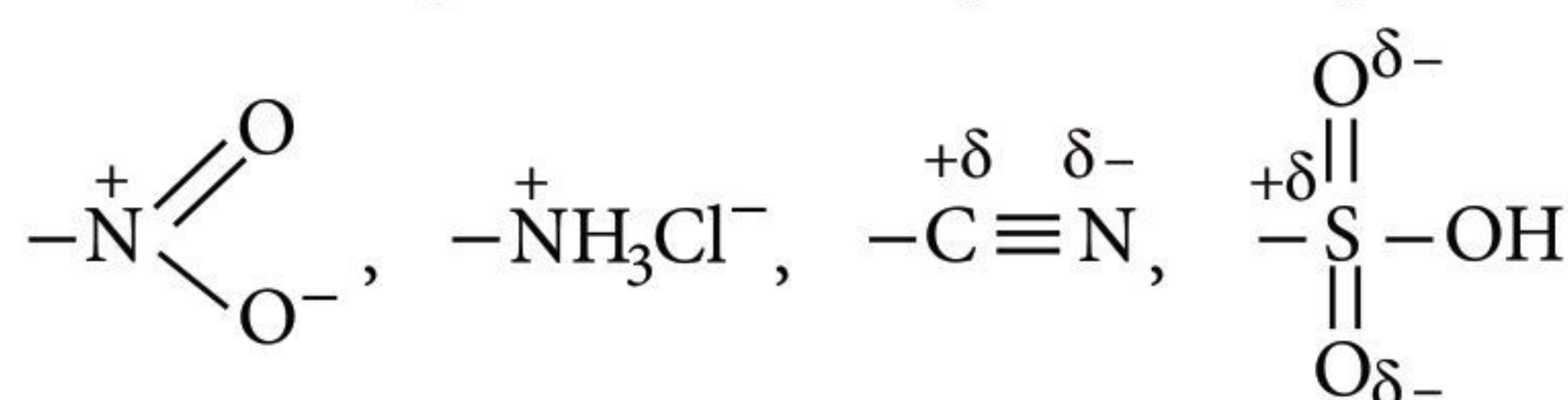
Thus, there are two types of substituents.

(i) ***o, p*-Directing groups** : The substituents or groups which direct the incoming group to *ortho* and *para* positions are called *o, p*-directing groups. For example, $-R$ (alkyl), $-C_6H_5$, $-OH$, $-SH$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOR$, $-OR$ (alkoxy), $-Cl$, $-Br$, $-I$.

- In general electron-donating groups are *o, p*-directing. Halogens ($-Cl$, $-Br$, $-I$) and nitroso group ($-N=O$) are exception to it which are electron withdrawing but *o, p*-directing.

(ii) ***m*-Directing groups** : The substituents or groups which direct the incoming group to the *meta* position are called *m*-directing groups. For example, $-SO_3H$, $-COOH$, $-COOR$, $-COR$, $-CHO$, $-CCl_3$, $-CF_3$, $-CN$, $-COCl$, $-NO_2$, $-NH_3^+$, $-NH_2R^+$, $-NR_3^+$, $-SO_2Cl$, $-NH_3Cl$, etc.

- In general all electron withdrawing groups are *m*-directing. Substituents which have a positive charge on the atom directly attached to the benzene ring are *m*-directing. For example,



The effect of substituents on the reactivity of a benzene ring towards electrophilic substitution

Activating substituents	Most activating		
	$-NH_2$ $-NHR$ $-NR_2$ $-OH$ $-OR$	strongly activating	ortho/para directing
	$-HNC(=O)R$ $-OC(=O)R$	moderately activating	
	$-R$ $-Ar$ $-CH=CR_2$	weakly activating	
Standard of comparison = $-H$			
	$-F$ $-Cl$ $-Br$ $-I$	weakly deactivating	
	$-CH=O$ $-C(=O)R$ $-COR$ $-COOH$ $-CCl_3$ $-C\equiv N$ $-SO_3H$ $-NH_3^+$ $-NH_2R^+$ $-NHR_2^+$ $-NR_3^+$ $-NO_2$	moderately deactivating	meta directing
		strongly deactivating	
Deactivating substituents	Most deactivating		



COMIC CAPSULE



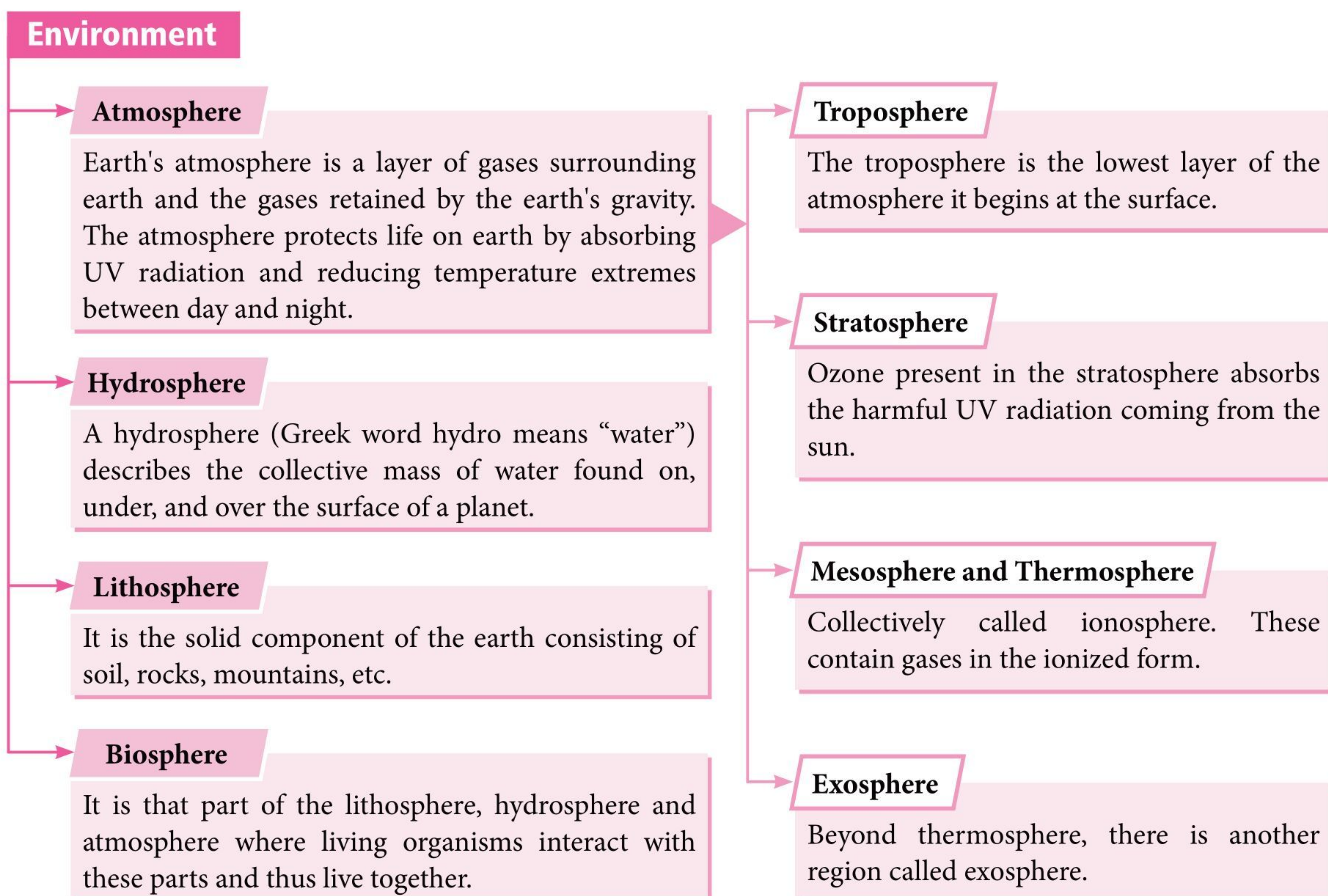
Environmental Chemistry

- *Environmental chemistry* is the scientific study of the chemical and biochemical phenomena that occur in natural places. It can be defined as, the study of the sources, reactions, transport, effects, and fates of chemical species in the air, soil, and

water environments; and the effect of human activity on these.

Earth's environment comprises of the following four major components :

1. Atmosphere
2. Hydrosphere
3. Lithosphere
4. Biosphere



Regions of the Atmosphere

	Region	Altitude from earth's surface (in km)	Temperature range (in °C)	Gases/Species present
(i)	Troposphere	0-10	Decreases from 15 to -56	N ₂ , O ₂ , CO ₂ , H ₂ O vapour
(ii)	Stratosphere (or ozonosphere)	10-50	Increases from -56 to -2	N ₂ , O ₂ , O ₃ , O-atoms
(iii)	Mesosphere	50-85	Decreases from -2 to -92	N ₂ , O ₂ ⁺ , NO ⁺
(iv)	Thermosphere	85-500	Increases from -92 to 1200	O ₂ ⁺ , O ⁺ , NO ⁺ , e ⁻

ENVIRONMENTAL POLLUTION AND POLLUTANTS

Any undesirable change in our surroundings that has harmful effects on plants, animals and human beings is called *environmental pollution*. Any substance which causes pollution is called pollutant.

Types of Pollutants

Pollutants can be classified in different ways as follows :

- **Primary and secondary pollutants**
 - **Primary pollutants** are those which remain as such after their formation. For example, nitric oxide (NO), SO₂, NO₂, CO, hydrocarbons etc.
 - **Secondary pollutants** are formed from the primary pollutants in the atmosphere or hydrosphere. For example, hydrocarbons and oxides of nitrogen react together photochemically to form certain compounds (e.g., PAN i.e., peroxyacetyl nitrates) which act as secondary pollutants.
- **Degradable and non-degradable pollutants**
 - **Degradable pollutant** degrades after some time either automatically (e.g., by heat) or through action of micro-organisms (biodegradable, e.g., sewage).
 - **Non-degradable pollutant** does not degrade or break down into harmless material, e.g., DDT, plastics.

ATMOSPHERIC OR AIR POLLUTION

Air pollution is generally limited to troposphere and stratosphere.

Tropospheric Pollution

- Major gaseous and particulate pollutants responsible for tropospheric pollution are as follows :

Oxides of Sulphur

- Sulphur dioxide is a corrosive acidic gas which produces acid rain.
SO_x : SO₂ and SO₃ forms H₂SO₄ and cause acid rain.

Oxides of Nitrogen

- Major sources of nitrogen oxides are high temperature combustion processes, denitrifying bacteria, etc.
NO_x : NO and NO₂ get converted into HNO₃ causing acid rain.

Hydrocarbons

- They are majorly produced naturally (e.g., marsh gas) as well as due to incomplete combustion of automobile fuel.

Polynuclear aromatic hydrocarbons (PAH) are carcinogenic. Methane (marsh gas) is a greenhouse gas.

Oxides of Carbon

- Two major pollutant oxides of carbon are carbon monoxide and carbon dioxide.
 - **Carbon monoxide** : Carbon monoxide (CO) is a toxic gas which is emitted into the atmosphere by incomplete combustion of coal and firewood and by oxidation of hydrocarbons and other organic compounds.
 - **Carbon dioxide** : CO₂ is released into atmosphere by respiration, burning of fossil fuels, forest fires, decomposition of limestone in cement industry, etc. It is a greenhouse gas, concentration of which is constantly rising.

Greenhouse Effect and Global Warming

- The **greenhouse effect** is the process in which the emission of infrared radiation by the atmosphere warms the earth surface.

Earth absorbs energy from sunlight entering the atmosphere and emits energy out to space in the form of infrared rays. The incoming sunlight, which is radiation with a shorter wavelength, travels unobstructed through the atmosphere (unless hitting a cloud) because this short wave radiation have a wavelength that is not in the absorption range of atmospheric gases. On the other hand, the outgoing radiation emitted by the surface is at a wavelength that is the absorption range of many atmospheric gases, including carbon dioxide, methane, and water vapour.

These radiations are thus gets locked in the earth's atmosphere.

This results in the steady increase in the temperature of the earth resulting in **global warming**.

Greenhouse gases include carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapours.

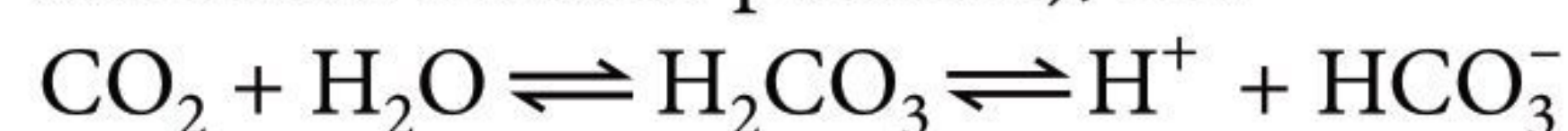
Acid Rain

- Rain water normally has a pH of 5.6 due to dissolution of CO_2 present in the atmosphere.

Particulate Matter

- Particulate pollutants are small solid particles and liquid droplets suspended in air. These are released in atmosphere by volcanic eruption, grinding, blowing

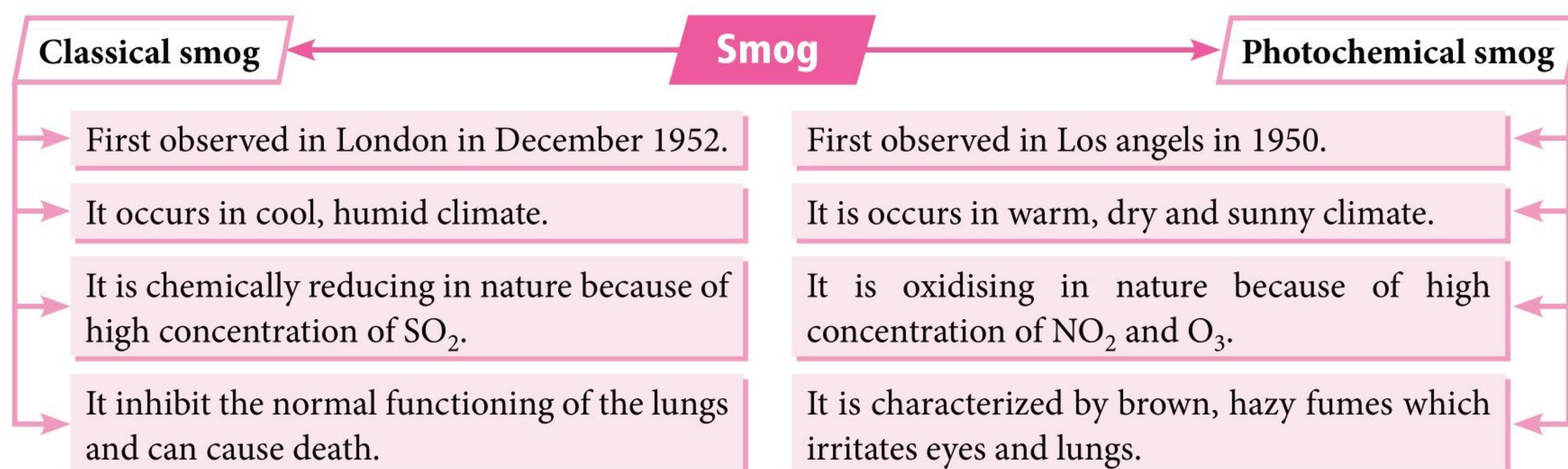
of dust, incomplete combustion of fossil fuels (which introduce soot), combustion of high-ash fossil fuels (which introduce fly ash), finishing of metals (which introduce metallic particles), etc.



When this pH falls below 5.6, the rain water becomes acidic. It is caused due to presence of acidic gases into the atmosphere.

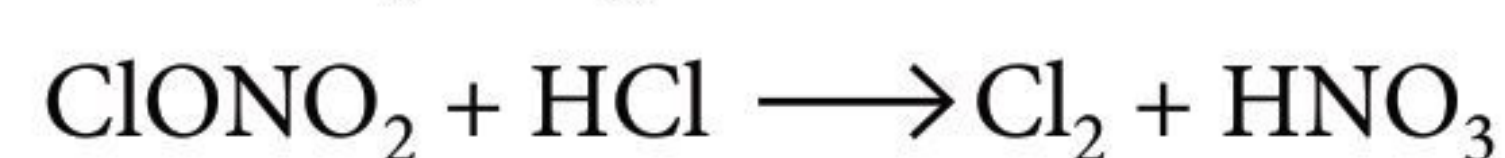
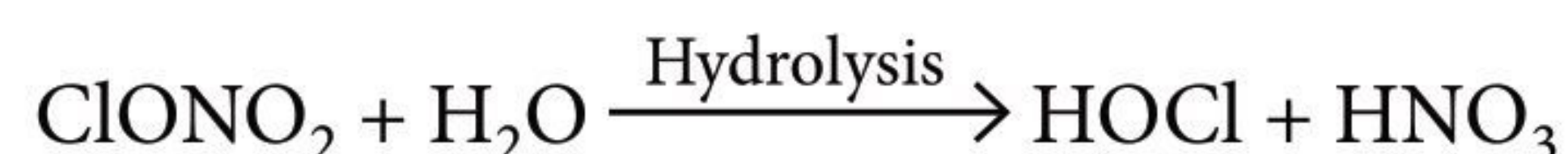
Smog

- Smog is a combination of smoke and fog.

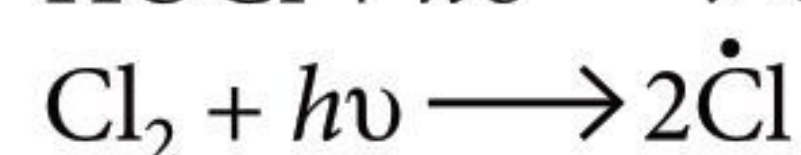
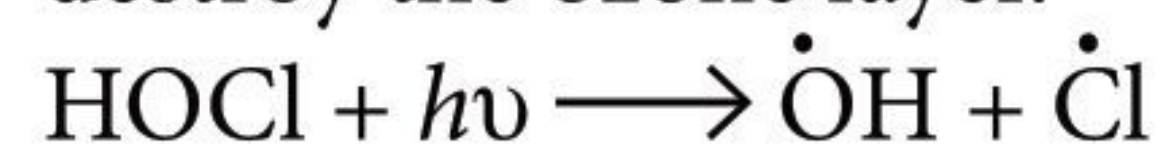


OZONE DEPLETION

- At higher altitudes stratosphere consists of a layer of ozone (O_3) which acts as an umbrella or shield for harmful ultraviolet radiations coming from sun and thus protect us from their harmful effects such as skin cancer.
- Nitric oxide and chlorofluorocarbons are found to be most responsible for depletion of ozone layer.

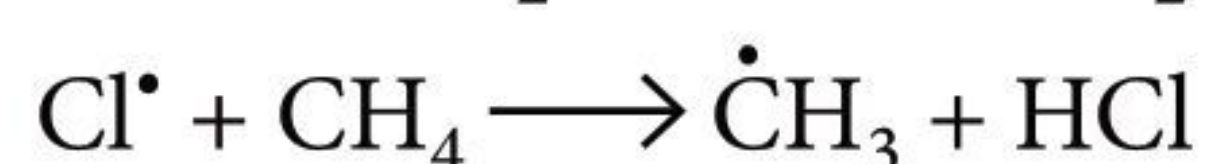
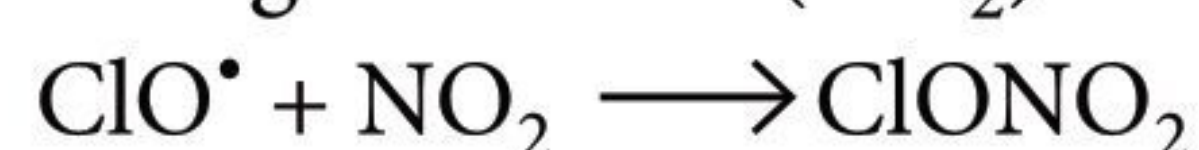


During spring, the sun shines over Antarctica and HOCl and Cl_2 formed in above reactions undergo photolysis to form reactive chlorine atoms which destroy the ozone layer.



Ozone Depletion Over Antarctica

- In most parts of the stratosphere, ClO^\bullet reacts with nitrogen dioxide (NO_2) and hydrocarbons.



This prevents active chlorine species from reacting with more ozone, slowing down ozone depletion.

In Antarctica, the climatic conditions are quite different. In winters, there are special types of clouds called **Polar Stratospheric Clouds** (PSCs) composed of either supercooled nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) (Type I PSC) or ice (Type II PSC). These clouds convert chlorine nitrate and HCl formed in above reactions into HOCl and Cl_2 through the following reactions :

WATER POLLUTION

- Water pollution is the introduction of chemical, physical or biological material into fresh or ocean waters that degrades the quality of the water and affects the organisms living in it. Some important sources of water pollution include industrial effluents, mining and agricultural waste, sewage disposed, domestic waste and organic waste etc. Pollutants may be microbiological or chemical in nature.

Eutrophication

- Eutrophication is a process whereby water bodies, receive excess nutrients that stimulate excessive plant growth (algae, periphyton attached algae, and other plant weeds). This enhanced plant growth,

often called an algal bloom, reduces dissolved oxygen in the water.

Biochemical Oxygen Demand (BOD)

- The total amount of oxygen in milligrams consumed by microorganisms in decomposing the waste (both inorganic and organic) in one litre of water at 20°C during a five day period is called biochemical oxygen demand (BOD) of the water.

Chemical Oxygen Demand (COD)

- Chemical oxygen demand refers to the amount of oxygen, expressed in parts per million, consumed under specific conditions in the oxidation of the organic and oxidizable inorganic matter contained in industrial waste water.

SOIL POLLUTION

- Soil pollution is defined as, the build-up of persistent toxic compounds, chemical salts, radioactive

materials, or disease causing agents, in soils which have adverse effects on plant growth and animal health.

Sources of Soil Pollution

- Insecticides, herbicides, fungicides, industrial effluents/wastes and radioactive pollutant etc.

GREEN CHEMISTRY

- Green chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

Green chemistry refers to the redesign of chemical products and processes with the goal of reducing or eliminating any negative environmental or health effects. Examples of green chemistry projects include: finding non-toxic, non-volatile solvent substitutes, developing new catalysts and environmental friendly materials.



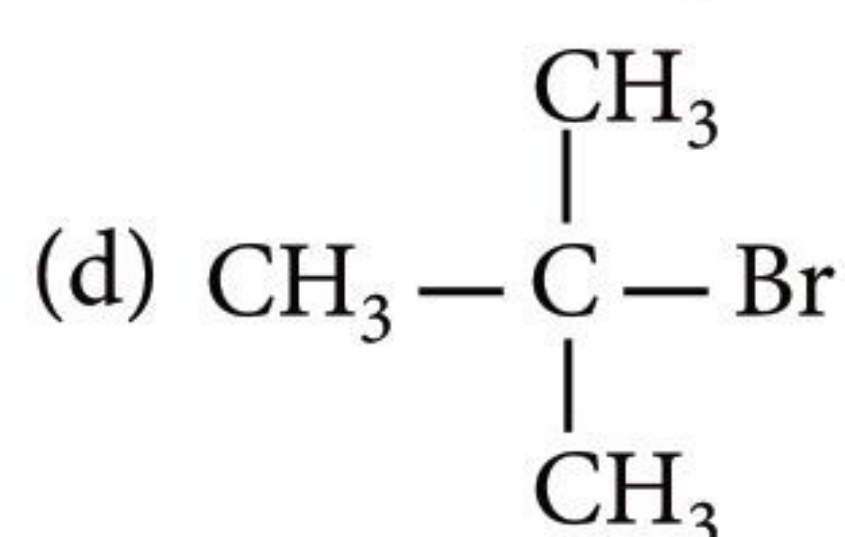
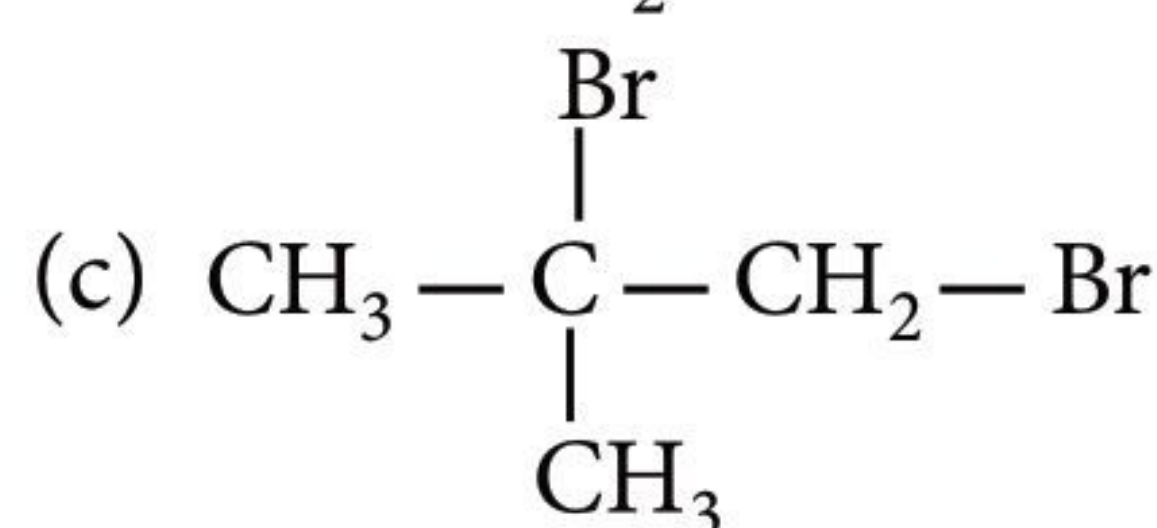
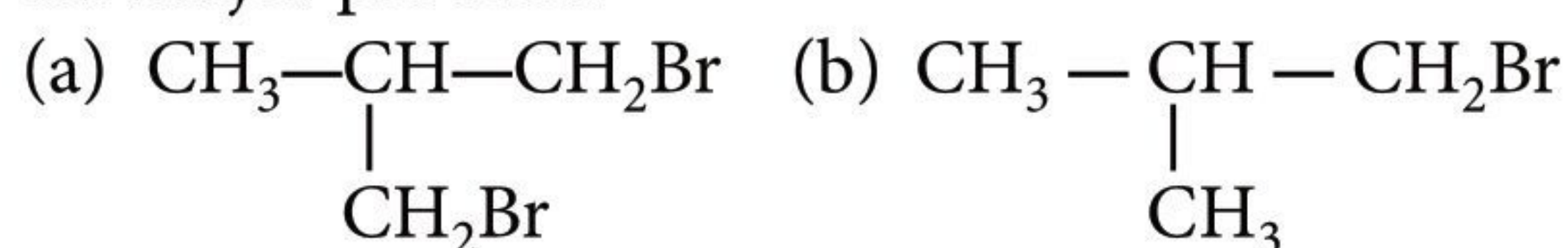
WRAP it up!

MCQs Type

1. N_2O resembles O_2 in which of the following characteristics?
(a) It is involved in production of photochemical smog.
(b) It is estimated quantitatively in organic compounds by Duma's method.
(c) It supports combustion.
(d) It is used to prevent growth of botulism bacteria in food.
2. The oxidation of benzene by V_2O_5 in the presence of air produces
(a) maleic anhydride (b) benzoic acid
(c) benzaldehyde (d) benzoic anhydride.
3. The point of temperature inversion between troposphere and ionosphere is called
(a) stratopause (b) mesopause
(c) tropopause (d) ionopause.
4. Presence of high concentration of ozone and smog in atmospheric air causes
(a) embrittlement of steel
(b) cracking of rubber products
(c) fading of dye on textiles
(d) damage of electrical insulator on high tension power line.
5. Use of chlorofluorocarbon is not encouraged because
(a) they are harmful to the eyes of people that use it
(b) they damage the refrigerators and air conditioners
(c) they eat away the ozone in the atmosphere
(d) they destroy the oxygen layer.
6. Allylic bromination of an olefin is
(a) nucleophilic substitution
(b) electrophilic substitution
(c) free radical substitution
(d) electrophilic addition.
7. Fish die in water bodies polluted by sewage due to
(a) pathogens (b) decrease in BOD
(c) decrease in D.O. (d) foul smell.
8. Which of the following statements is false?

- (a) The main reason for river water pollution is industrial and domestic sewage discharge.
- (b) Surface water contains a lot of organic matter, mineral nutrients and radioactive materials.
- (c) Oil spill in sea water causes heavy damage to fishery.
- (d) Oil slick in sea water increases D.O. value.

9. Excess of isobutane on reaction with Br_2 in presence of light at 125°C gives which one of the following, as the major product?



(JEE Main 2021)

10. The product(s) obtained via oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-butyne would be

- (a) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$
- (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$
- (c) $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCHO}$
- (d) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$

11. Acid rains are produced by

- (a) excess NO_2 and SO_2 from burning fossil fuels
- (b) excess production of NH_3 by industry and coal gas
- (c) excess release of carbon monoxide by incomplete combustion
- (d) excess formation of CO_2 by combustion and animal respiration.

12. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because

- (a) both are highly ionic
- (b) one is oxidising and the other is reducing
- (c) one of the steps is endothermic in both cases
- (d) all steps are exothermic in both cases.

13. Which of the following is not correct about carbon monoxide?

- (a) It forms carboxyhaemoglobin.
- (b) It reduces oxygen carrying ability of blood.

- (c) The carboxyhaemoglobin (haemoglobin bound to CO) is less stable than oxyhaemoglobin.
- (d) It is produced due to incomplete combustion.

(NEET 2020)

14. The product of $\text{CH}\equiv\text{CH} \xrightarrow[\text{Hg}^{2+}]{\text{CH}_3\text{COOH}}$ is

- (a) $\text{CH}_2=\text{CHCl}$ (b) $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$
- (c) CH_3CHO (d) $\text{CH}_3\text{CH}_2\text{CHO}$

15. Which one is incorrect name?

- (a) Propyne (b) But-2-yne
- (c) Pent-3-yne (d) But-1-yne

16. Which of the following statements is false?

- (a) Lower the concentration of D.O., the more polluted is the water sample.
- (b) The tolerable limit of lead in drinking water is 50 ppb.
- (c) Water is considered pure if it has BOD less than 5 ppm.
- (d) In COD determination, the pollutants resistant to microbial oxidation are not oxidised by oxidising agent like $\text{K}_2\text{Cr}_2\text{O}_7$.

17. Match the lists I with II and pick the correct matching from the codes given below:

List I				List II	
(A) Peroxy acetyl nitrate				1. Water pollution	
(B) Polycyclic aromatic hydrocarbons				2. Global warming	
(C) Pathogens				3. Photochemical smog	
(D) Indigo				4. Carcinogens	
(E) IR active molecules				5. Vat dye	
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
(a)	3	4	1	5	2
(b)	1	2	3	4	5
(c)	3	5	1	2	4
(d)	5	3	1	2	4

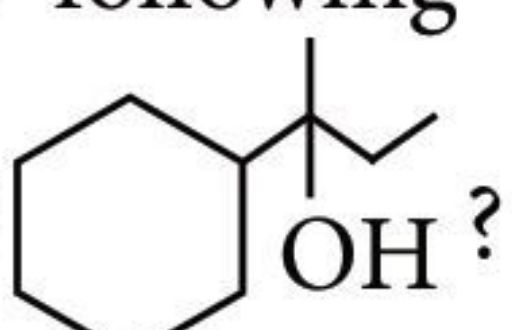
18. The compound X (C_5H_8) reacts with ammoniacal AgNO_3 to give a white precipitate, and on oxidation with hot alkaline KMnO_4 gives the acid,

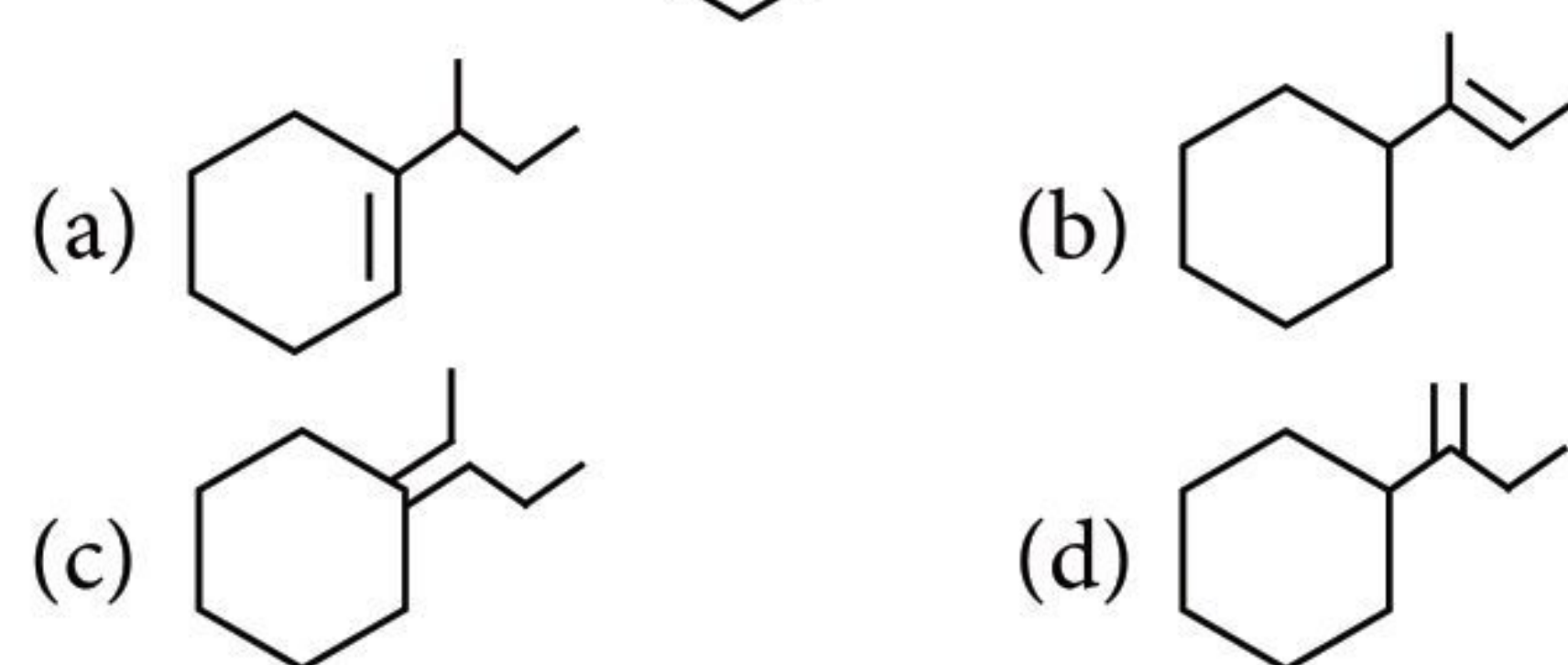
$(\text{CH}_3)_2\text{CHCOOH}$. Therefore, X is

- (a) $\text{CH}_2=\text{CHCH}=\text{CHCH}_3$
- (b) $\text{CH}_3(\text{CH}_2)_2\text{C}\equiv\text{CH}$
- (c) $(\text{CH}_3)_2\text{CH}-\text{C}\equiv\text{CH}$
- (d) $(\text{CH}_3)_2\text{C}=\text{C}=\text{CH}_2$

19. When *neo*-pentyl bromide is subjected to Wurtz reaction, the product formed is
 (a) 2,2,4,4-tetramethylhexane
 (b) 2,2,4,4-tetramethylpentane
 (c) 2,2,5,5-tetramethylhexane
 (d) 2,2,3,3-tetramethylhexane.
20. Dihedral angle of least stable conformer of ethane is
 (a) 0° (b) 120°
 (c) 180° (d) 60° (NEET 2021)

21. Which of the following is not the product of

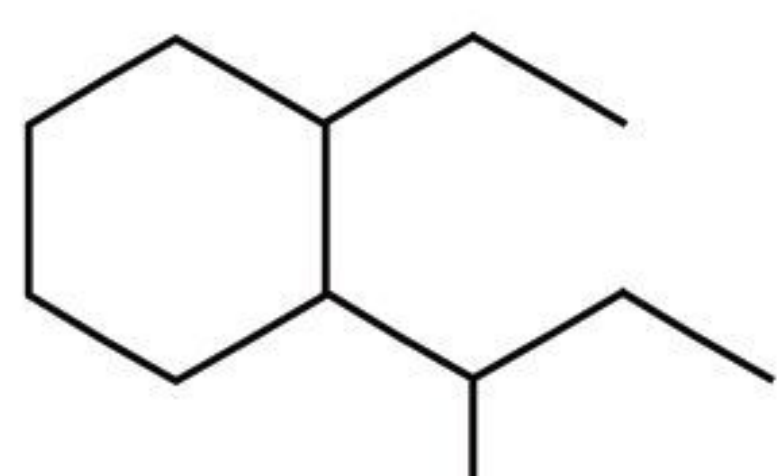
dehydration of  ?



22. Benzene has
 (a) 3 delocalized electrons
 (b) 4 delocalized electrons
 (c) 6 delocalized electrons
 (d) 12 delocalized electrons.
23. Toluene on reaction with *N*-bromosuccinimide gives
 (a) *p*-bromomethylbenzene
 (b) *o*-bromomethylbenzene
 (c) phenylbromomethane
 (d) *m*-bromomethylbenzene.
24. Alkane with octane number 100 is
 (a) 2, 2, 4- trimethylpentane
 (b) hexane
 (c) heptane
 (d) butane.
25. Thermal power plants can lead to
 (a) acid rain
 (b) blue baby syndrome
 (c) ozone layer depletion
 (d) eutrophication. (JEE Main 2020)

NUMERICAL VALUE TYPE

26. Number of 2° carbons in the given compound is ____.

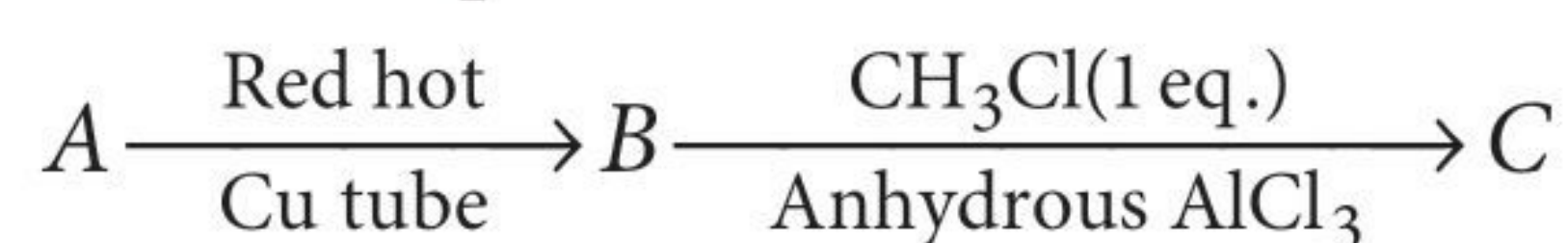


27. The number of acyclic structural isomers (including, geometrical isomers) for pentene are ____.

28. Compound (A) contained 88.89% C and 11.11% H. It gave a white precipitate with ammoniacal silver nitrate. Complete hydrogenation of (A) gave another compound (B) with molecular weight 112. Oxidation of (B) gave an acid with equivalent weight 128. Decarboxylation of this acid gave cyclohexane. The number of *sp* hybridised carbon atoms in (A) are ____.

29. 11.14 g of 1,1,2,2-tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal AgNO_3 . The mass of precipitate (in g) obtained is ____.

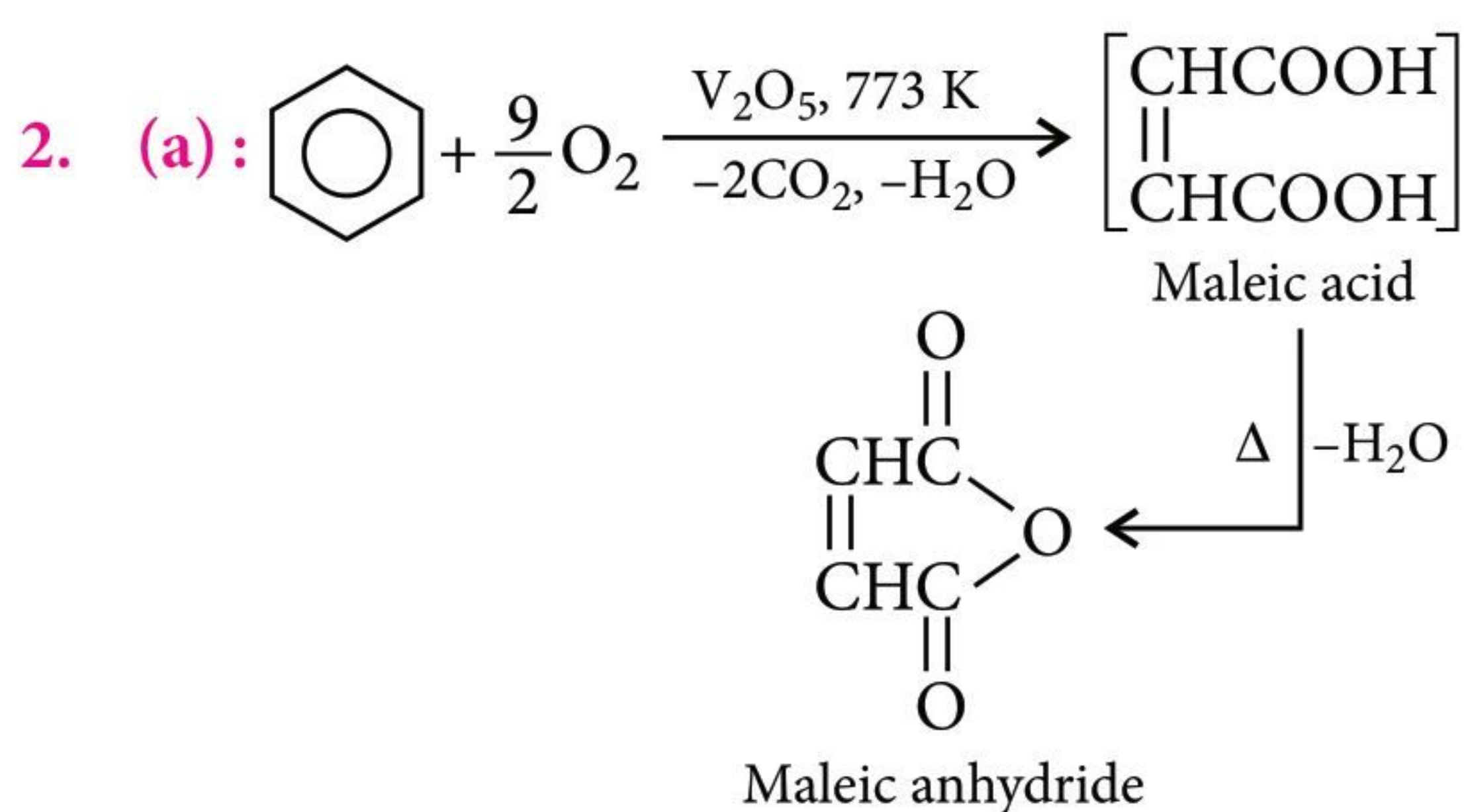
30. In the following sequence of reactions, the maximum number of atoms present in molecule 'C' in one plane is ____.



(A is a lowest molecular weight alkyne.)

SOLUTIONS

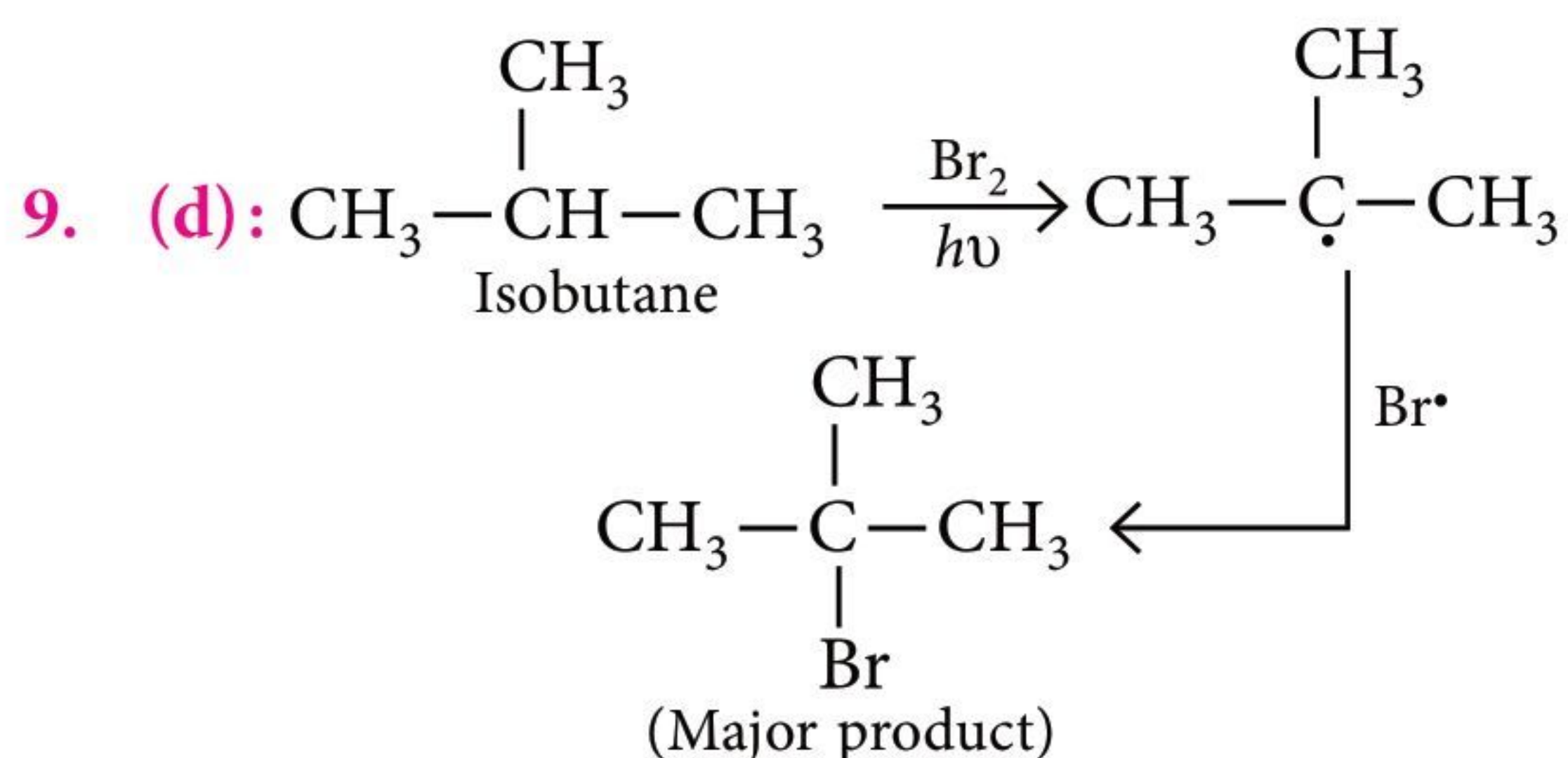
1. (c) : It does so because it decomposes to molecular nitrogen and oxygen when heated. So, it support combustion, $2\text{N}_2\text{O} \longrightarrow 2\text{N}_2 + \text{O}_2$



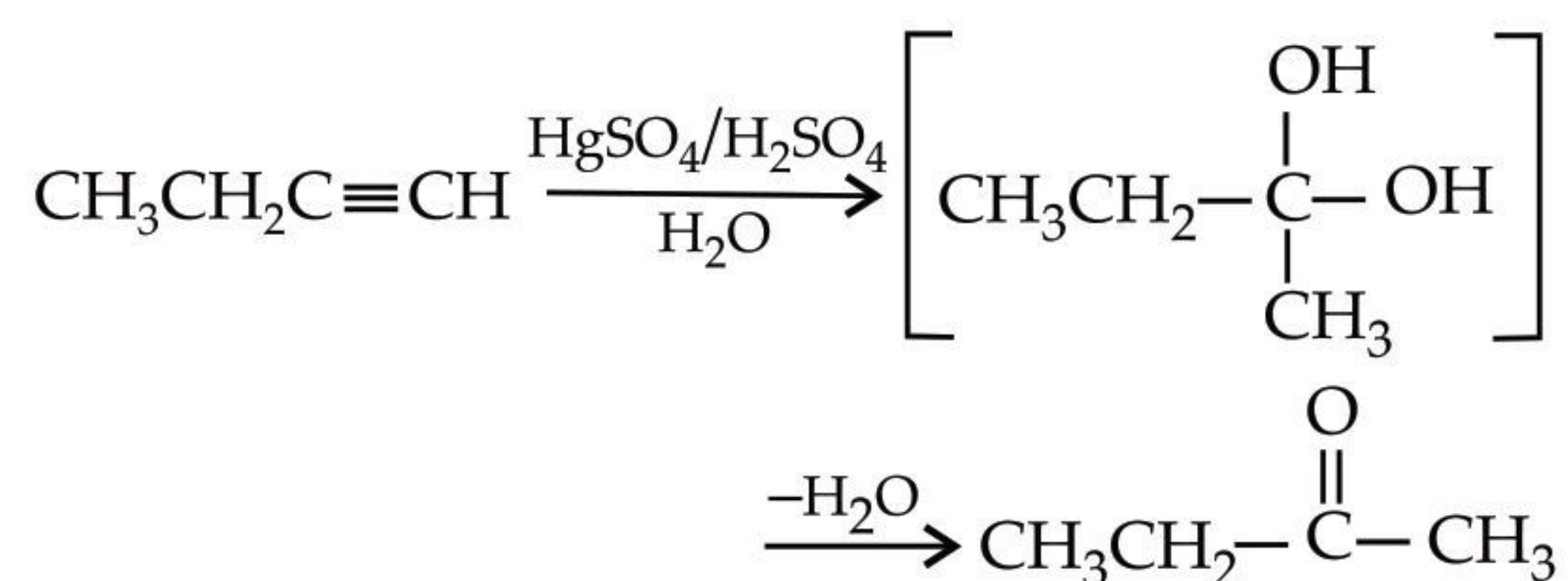
3. (c) : In the region lower to tropopause temperature decreases with increase of altitude whereas in the region upper to tropopause temperature increases with increase of altitude.
4. (b)
5. (c) : Chlorofluorocarbon is used in air-conditioning and in domestic refrigerators for cooling purposes. But, it is responsible for ozone depletion. So its use is not encouraged.
6. (c) : It is a free radical substitution reaction.

7. (c) : Microorganisms from sewage consume all dissolved oxygen and fish get deprived of this oxygen and ultimately die.

8. (d) : Oil slick (layer) in sea water decreases D.O. value.



10. (a) : Hydration of alkynes via mercuration occurs according to Markownikoff's rule.



11. (a) : Acid rains are produced by excess NO_2 and SO_2 from burning fossil fuels.

12. (c) : One of the steps in the reaction is endothermic.

13. (c) : The carboxyhaemoglobin is about 300 times more stable than oxyhaemoglobin.

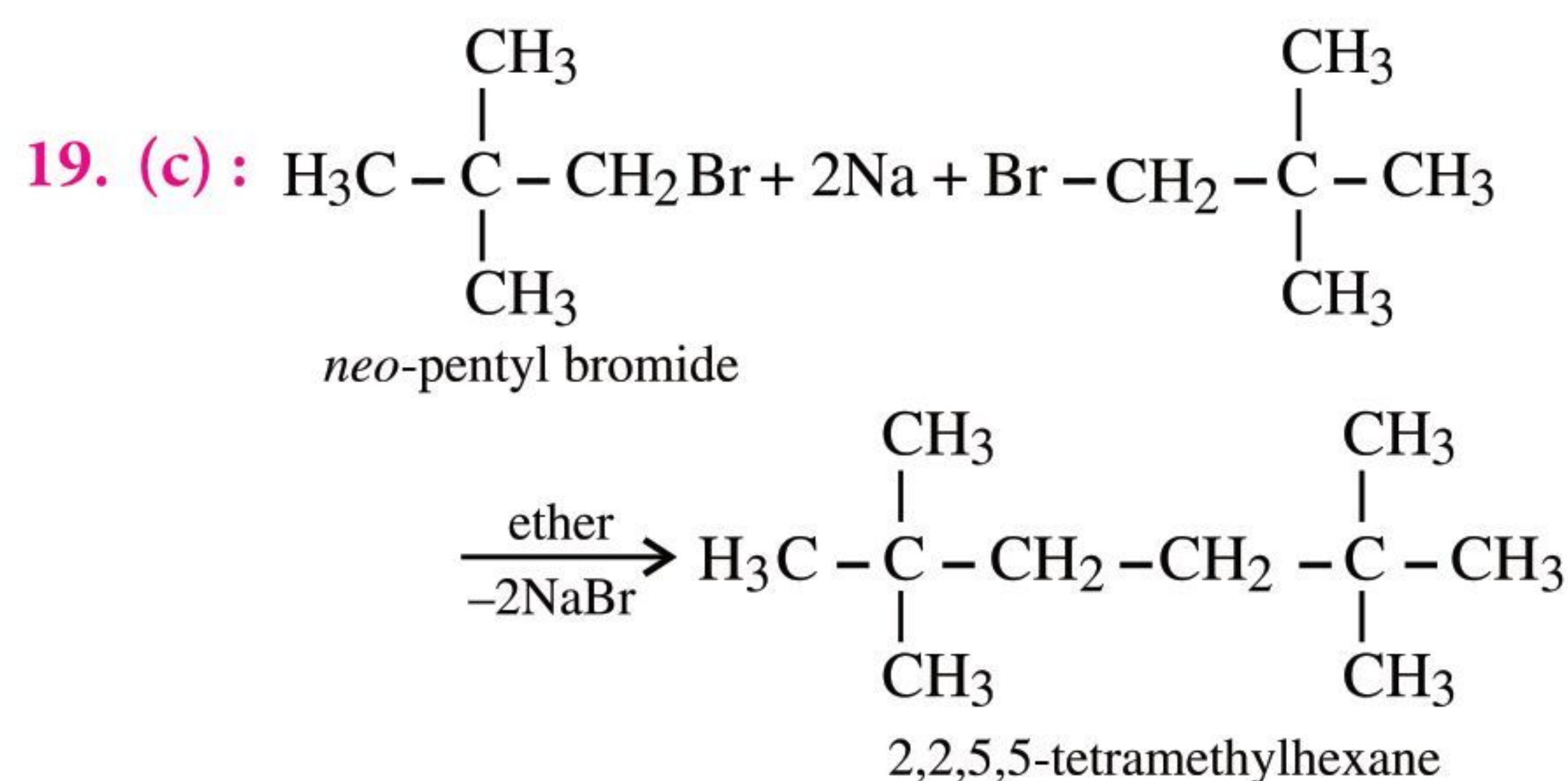
14. (b)

15. (c) : Correct name is pent-2-yne.

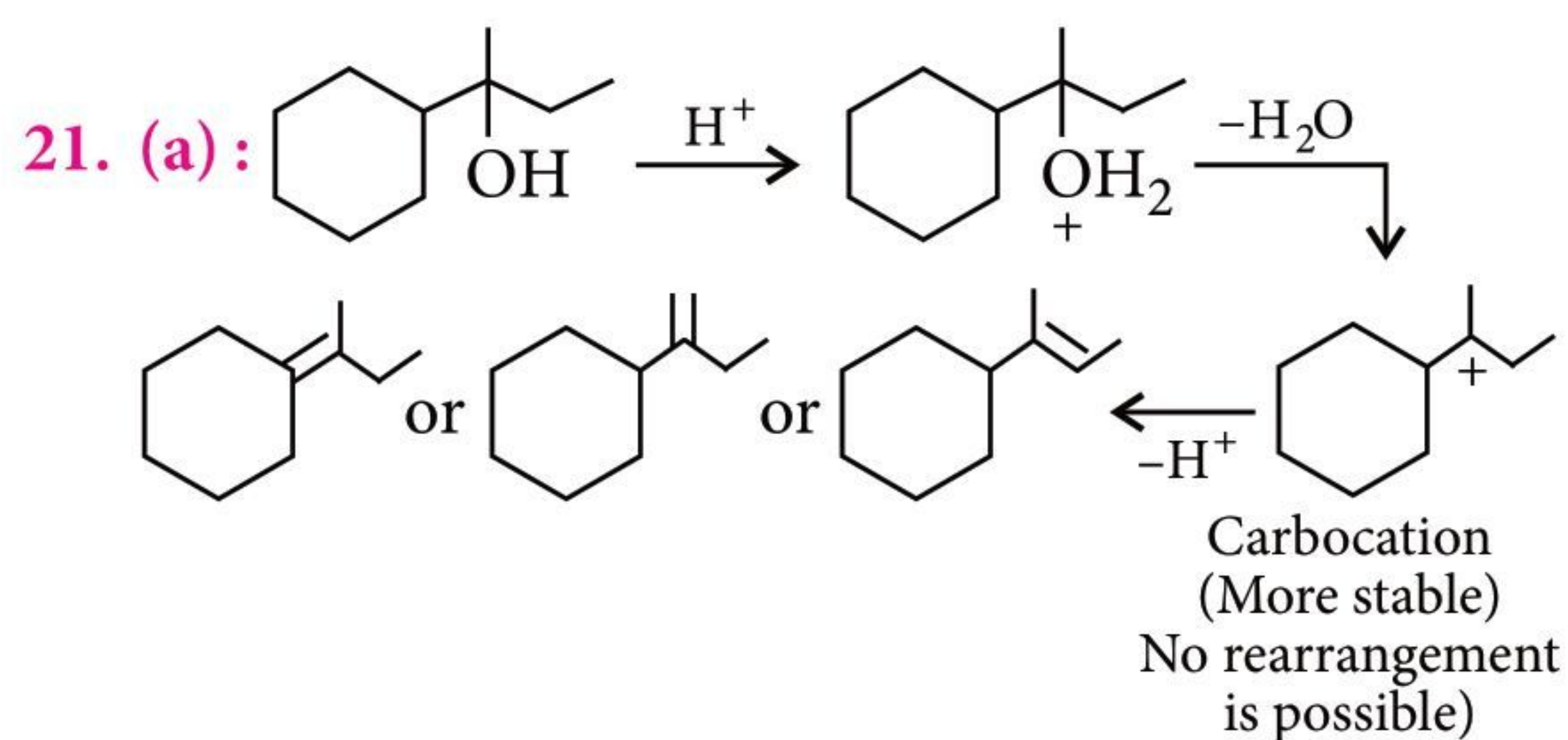
16. (d) : In COD determination, both organic and inorganic pollutants are oxidised by oxidising agent like $\text{K}_2\text{Cr}_2\text{O}_7$.


17. (a) : Peroxy acetyl nitrate (PAN) is main component of photochemical smog, polycyclic aromatic hydrocarbons are found to be carcinogenic in nature, pathogens are most serious water pollutants, indigo is a vat dye and IR active molecules result in global warming.

18. (c) : Since the compound X (C_5H_8) reacts with ammoniacal AgNO_3 to give a white precipitate, it must be a terminal alkyne, i.e., it should have $-\text{C}\equiv\text{CH}$ group. Further, since X gives $(\text{CH}_3)_2\text{CHCOOH}$ on oxidation, X must have $(\text{CH}_3)_2\text{CHC}\equiv\text{C}-$ group. Thus, the compound X is $(\text{CH}_3)_2\text{CHC}\equiv\text{CH}$.



20. (a) : Dihedral angle of least stable conformer of ethane is 0° . Magnitude of torsional strain depends upon the angle of rotation about C—C bond. This angle is also called dihedral angle or torsional angle. Of all the conformations of ethane, the staggered form has the least torsional strain while the eclipsed form has the maximum torsional strain.






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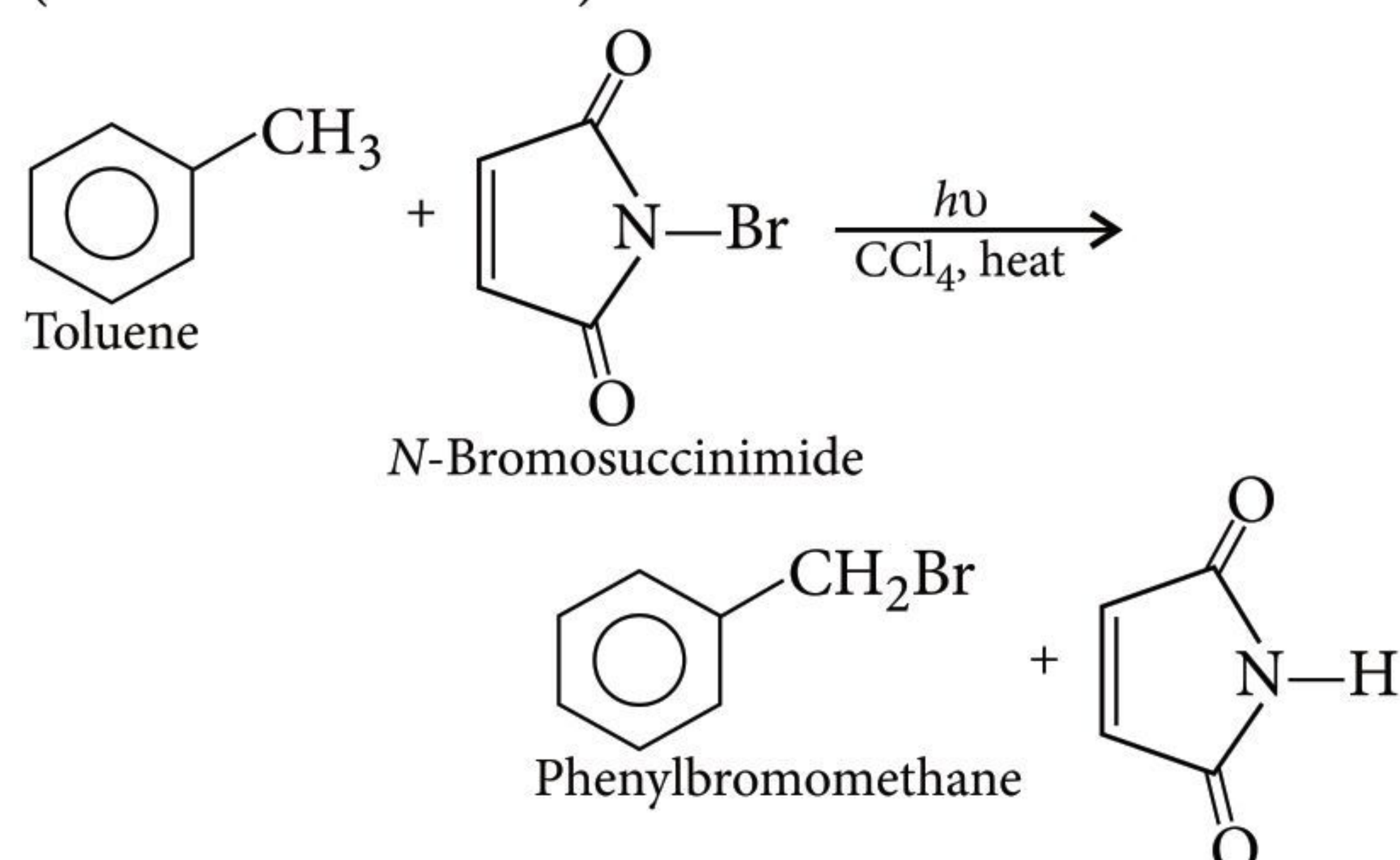


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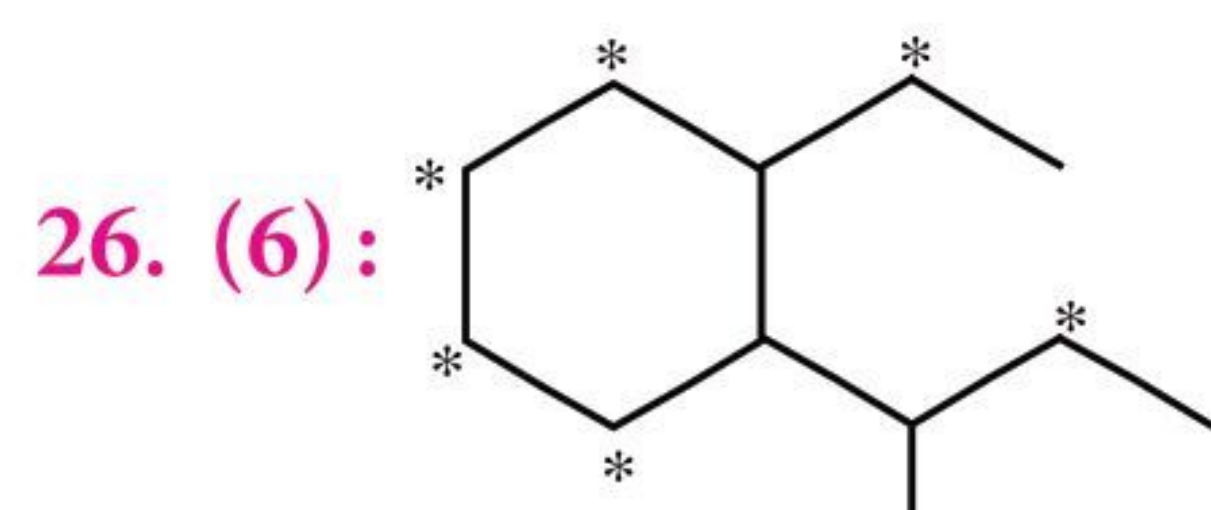
22. (c)

23. (c) : Allylic bromination takes place by NBS (free-radical reaction).



24. (a)

25. (a) : Thermal power plants produce large amount of nitrogen oxide and sulphur dioxide, the pollutants that cause acid rain.



Number of 2° carbons = 6

27. (6) : C—C—C—C=C (Pent-1-ene)



Pent-2-ene shows geometrical isomerism *i.e.*, *Cis* and *trans*. So, there are total 6 isomers possible for pentene.

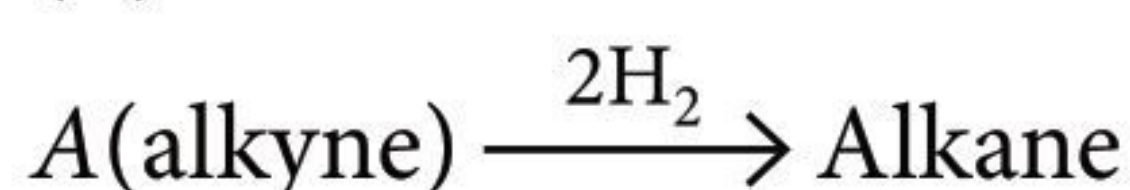
28. (2) : The empirical formula calculations

Element	%	Relative no. of atoms	Simplest ratio
C	88.89	7.41	1 or 2
H	11.11	11.11	1.49 or 3

∴ Empirical formula of (A) is C₂H₃.

Empirical formula weight = 27

Molecular weight of (A) can be determined by the fact that (A) is an alkyne as it gives white ppt. with ammoniacal AgNO₃ and on hydrogenation of (A), (B) is obtained with molecular weight 112.



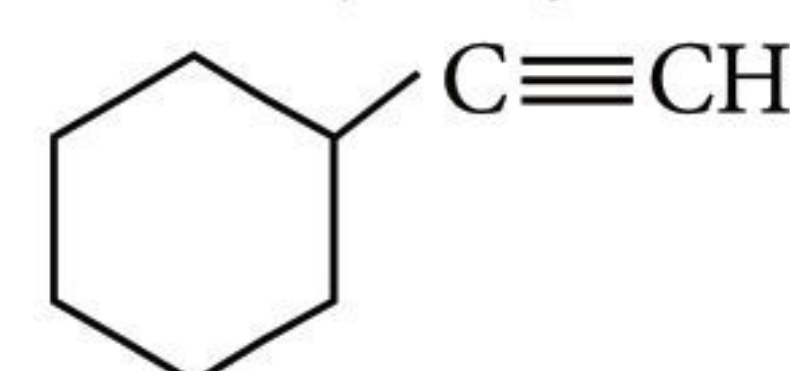
∴ Molecular weight of A = 112 - 4 = 108

Molecular formula of (A) is (C₂H₃)_n.

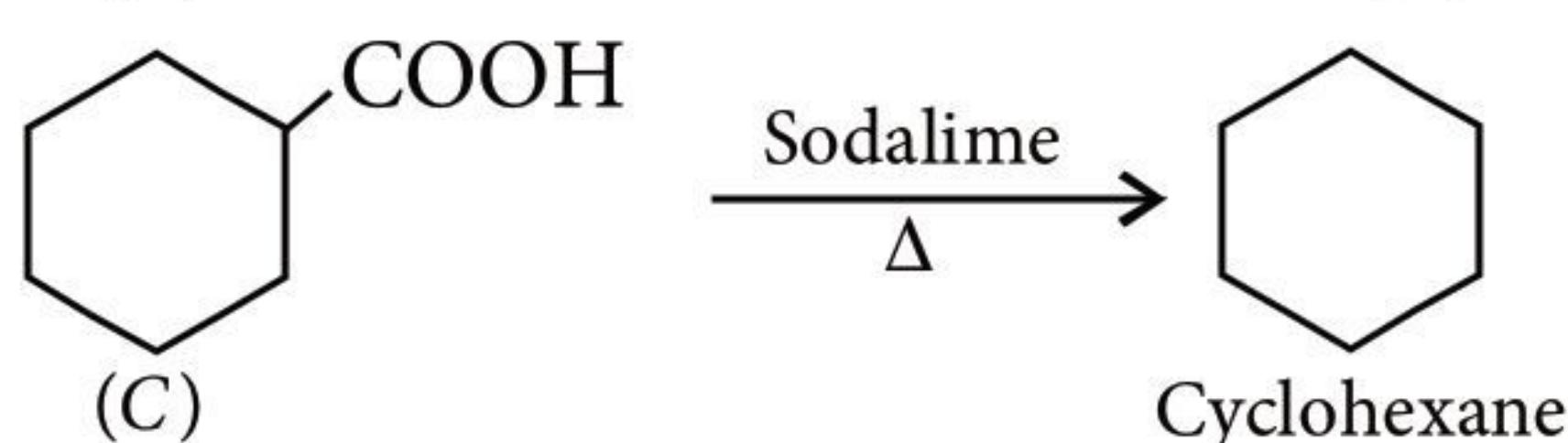
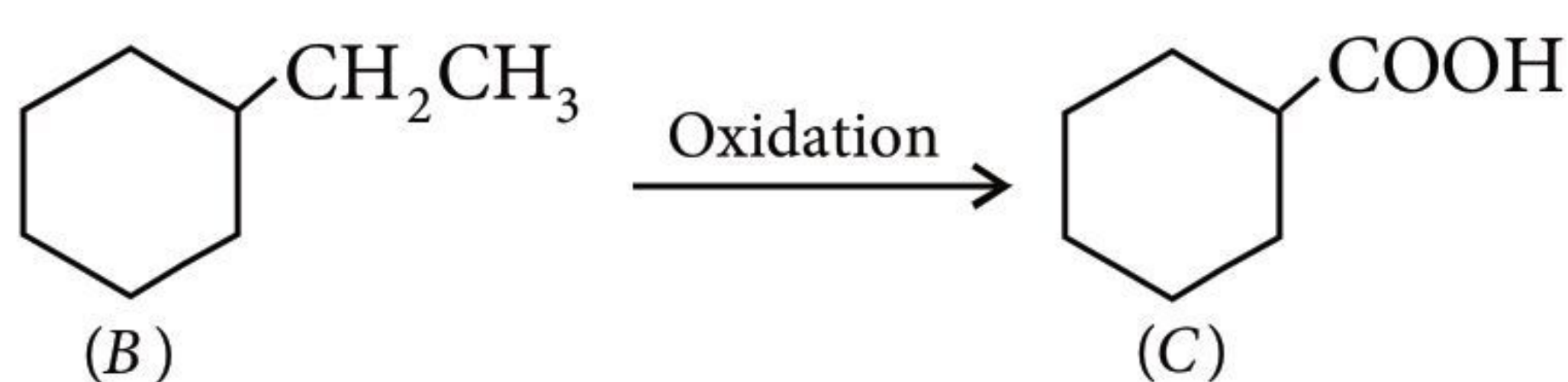
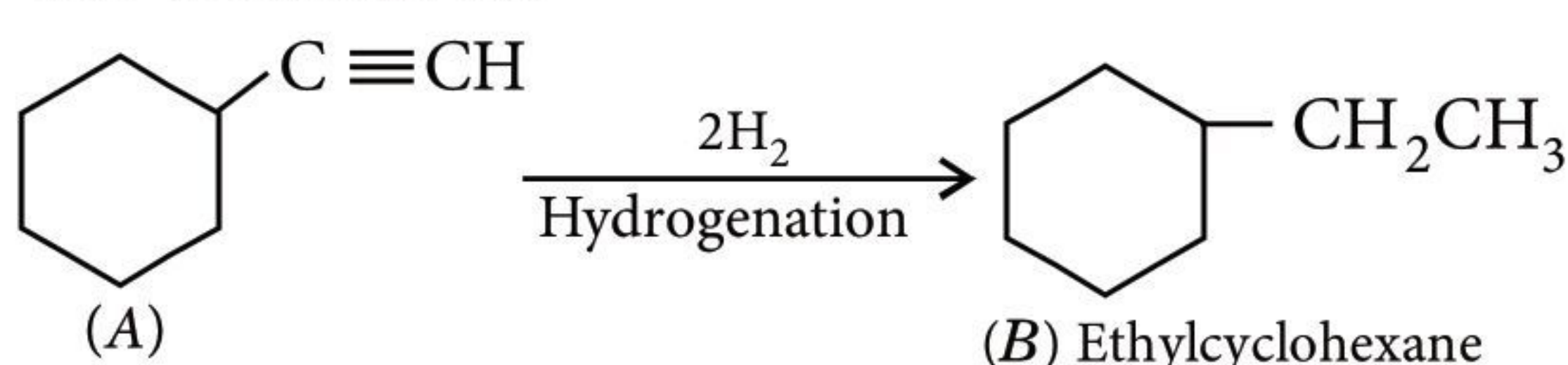
∴ $n = (108/27) = 4$

i.e., A is C₈H₁₂.

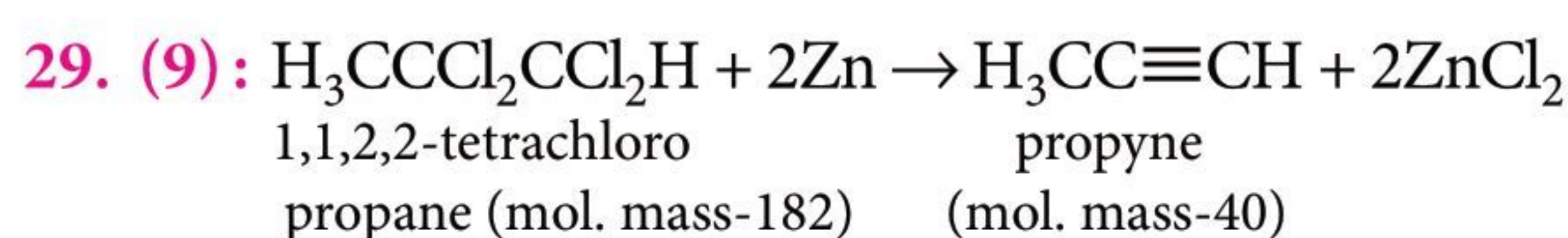
Keeping in view of its molecular formula, nature of terminal alkyne (A) may be given as



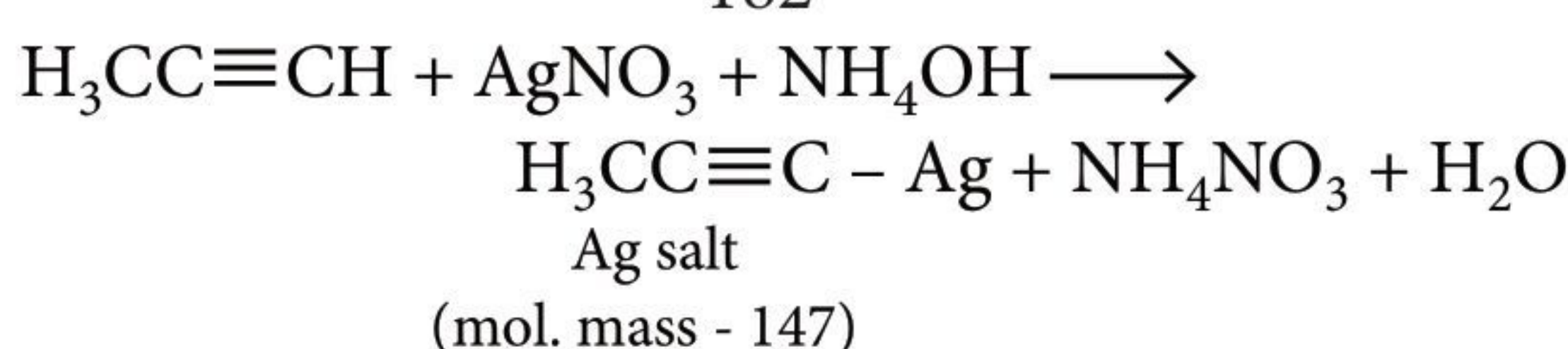
The reactions are



Number of C-atoms having *sp*-hybridisation in A is 2.

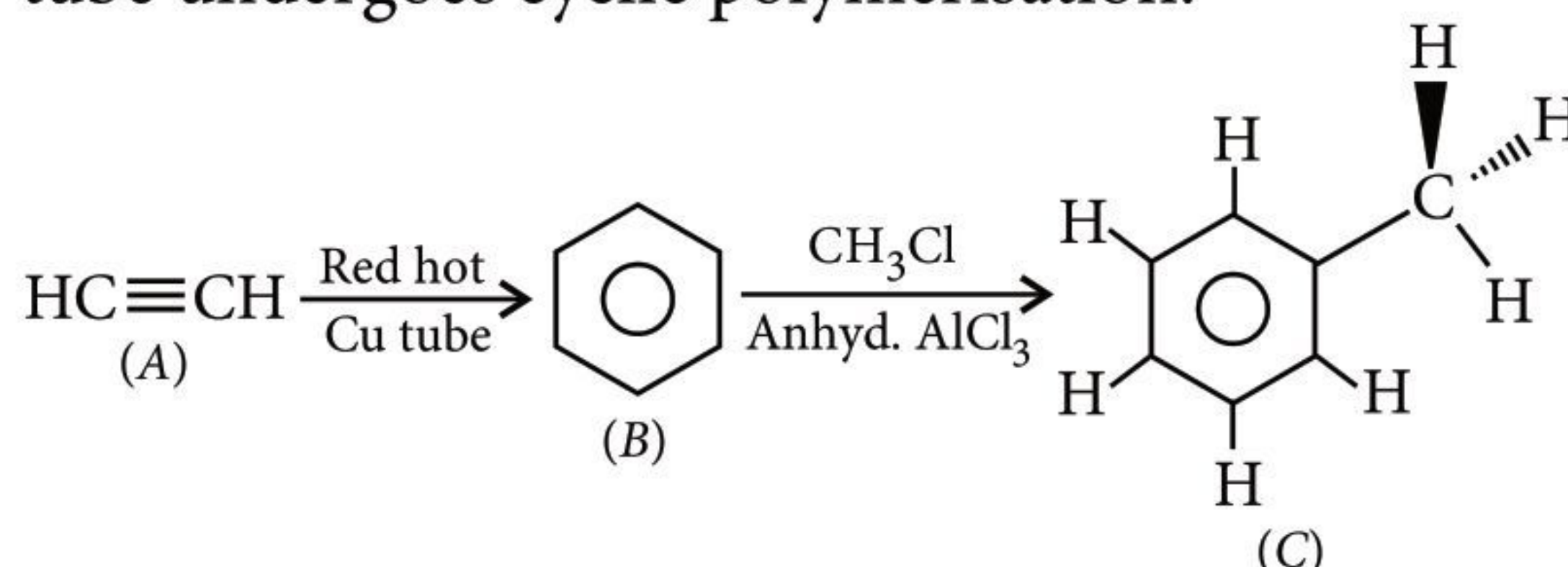


Mass of propyne obtained from 11.14 g of 1, 1, 2, 2-tetrachloropropane = $\frac{40}{182} \times 11.14 = 2.45$ g



Mass of precipitate obtained from 2.45 g of propyne = $\frac{147}{40} \times 2.45 = 9$ g.

30. (13) : The lowest molecular weight alkyne is ethyne HC≡CH, which on passing through red hot Cu tube undergoes cyclic polymerisation.



Thus, maximum number of atoms in one plane = 13.





CBSE

warm-up!

Term-II

CLASS-XI

Series-2

Chemical Thermodynamics | Equilibrium | Some *p*-Block Elements

Time Allowed : 2 hours

Maximum Marks : 35

General Instructions : Read the following instructions carefully.

1. There are 12 questions in this question paper with internal choice.
2. SECTION A - Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
3. SECTION B - Q. No. 4 to 11 are short answer questions carrying 3 marks each.
4. SECTION C - Q. No. 12 is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed.

SECTION - A

1. Give reasons for the following :
 - (i) CCl_4 is immiscible in water whereas, SiCl_4 is easily hydrolysed.
 - (ii) Carbon has a strong tendency for catenation as compared to silicon.
2. The heat of combustion of carbon to CO_2 at constant pressure is -393.5 kJ/mol . Calculate heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas.
3. At 25°C , K_p for the reaction : $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ has a value of 0.14 atm . Calculate the value of K_c in which the concentrations are measured in mol L^{-1} .

SECTION - B

4. Explain the following :
 - (i) PbO_2 is a stronger oxidising agent than SnO_2 .
 - (ii) HNO_3 can be stored in aluminium vessel while NaOH solution cannot.
 - (iii) Standard electrode potential values, E° for Al^{3+}/Al is -1.66 V and that of Tl^{3+}/Tl is $+1.26 \text{ V}$. Predict about the formation of

M^{3+} ion in solution and compare the electropositive character of the two metals.

OR

- (i) Explain why BF_3 exists but BH_3 does not.
 - (ii) Compare the B — F bond length in BF_3 and BF_4^- .
5. At 473 K , equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3} . If decomposition is depicted as :
$$\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}; \Delta_r H^\circ = 124.0 \text{ kJ mol}^{-1}$$
 - (a) What is the value of K_c for the reverse reaction at the same temperature?
 - (b) What would be the effect on K_c if (i) the pressure is increased (ii) the temperature is increased?

OR

- (a) The solubility product of $\text{Al}(\text{OH})_3$ is 2.7×10^{-11} . Calculate its solubility in g L^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u , $\log 3 = 0.4771$.)
 - (b) What happens to the ionic product of water when HCl is added to it?
6. (i) Explain why diamond is very hard while graphite is soft?

- (ii) Why trihalides of group 13 elements behave as Lewis acids?
- (iii) Why aluminium chloride exists as a dimer?

OR

- (i) Explain the trend of ionisation energy of the elements of group 14.
 - (ii) Graphite is a conductor of electricity but diamond is not. Explain.
 - (iii) Explain why the reactions with hydrochloric acid and sulphur dioxide show the oxidizing nature of PbO_2 .
7. (a) Equilibrium constant, K_c for the reaction

$$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$$
 at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} of N_2 , 2.0 mol L^{-1} of H_2 and 0.5 mol L^{-1} of NH_3 . Is the reaction at equilibrium? If not, in which direction the reaction tend to proceed to reach equilibrium?
- (b) The solubility product of $\text{Fe}(\text{OH})_3$ is 1×10^{-36} . What is the minimum concentration of OH^- ions required to precipitate $\text{Fe}(\text{OH})_3$ from a 0.001 M solution of FeCl_3 ?
8. Diborane is a potential rocket fuel which undergoes combustion according to the reaction

$$\text{B}_2\text{H}_{6(g)} + 3\text{O}_{2(g)} \longrightarrow \text{B}_2\text{O}_{3(s)} + 3\text{H}_2\text{O}_{(g)}$$
 From the following data, calculate the enthalpy change for the combustion of diborane.

$$2\text{B}_{(s)} + 3/2\text{O}_{2(g)} \longrightarrow \text{B}_2\text{O}_{3(s)}; \Delta H = -1273 \text{ kJ mol}^{-1}$$

$$\text{H}_{2(g)} + 1/2\text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}; \Delta H = -286 \text{ kJ mol}^{-1}$$

$$\text{H}_2\text{O}_{(l)} \longrightarrow \text{H}_2\text{O}_{(g)}; \Delta H = 44 \text{ kJ mol}^{-1}$$

$$2\text{B}_{(s)} + 3\text{H}_{2(g)} \longrightarrow \text{B}_2\text{H}_{6(g)}; \Delta H = 36 \text{ kJ mol}^{-1}$$
9. Arrange the following in increasing order of the property indicated :
- (a) SiCl_2 , GeCl_2 , SnCl_2 and PbCl_2 (stability)
 - (b) CO , SiO , SnO , GeO , PbO (basicity)
 - (c) SiF_4 , SiCl_4 , SiI_4 , SiBr_4 (stability)
10. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Calculate the value of q , w , ΔU and ΔH assuming ideal gas behaviour.
 ($\log 2 = 0.301$, $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, At. Wt. of $\text{Ar} = 40 \text{ g mol}^{-1}$)

OR

A heated copper block at 130°C loses 340 J of heat to the surroundings which are at room temperature of 32°C . Calculate

- (i) the entropy change of the system (copper block)
- (ii) the entropy change in the surrounding
- (iii) the total entropy change in the universe due to this process.

Assume that the temperature of the block and the surrounding remains constant.

11. Define Le-Chatelier's Principle.

For the given reaction, $2\text{H}_{2(g)} + \text{CO}_{(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$
 How is the equilibrium affected

- (i) addition of H_2
- (ii) removal of CO ?

SECTION - C

12. Read the passage given below and answer the questions that follow:

Gibbs energy or Gibbs function, G is given as

$$G = H - TS$$

Gibbs function, G is an extensive property and a state function. The equation, $\Delta G = \Delta H - T\Delta S$, is known as Gibbs—Helmoholtz equation.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

ΔG gives a criteria for spontaneity at constant pressure and temperature.

- (i) If ΔG is negative (< 0), the process is spontaneous.
- (ii) If ΔG is positive (> 0), the process is non-spontaneous.

- (a) Under what conditions will a reaction be spontaneous if both ΔH and ΔS are negative?
- (b) What will be the sign of ΔS for the following reaction?

$$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$$
- (c) State the second law of thermodynamics.
- (d) For a process $\Delta H = 280 \text{ kJ mol}^{-1}$ and $\Delta S = 140 \text{ J K}^{-1} \text{ mol}^{-1}$. What is the minimum temperature at which the process will be spontaneous?

OR

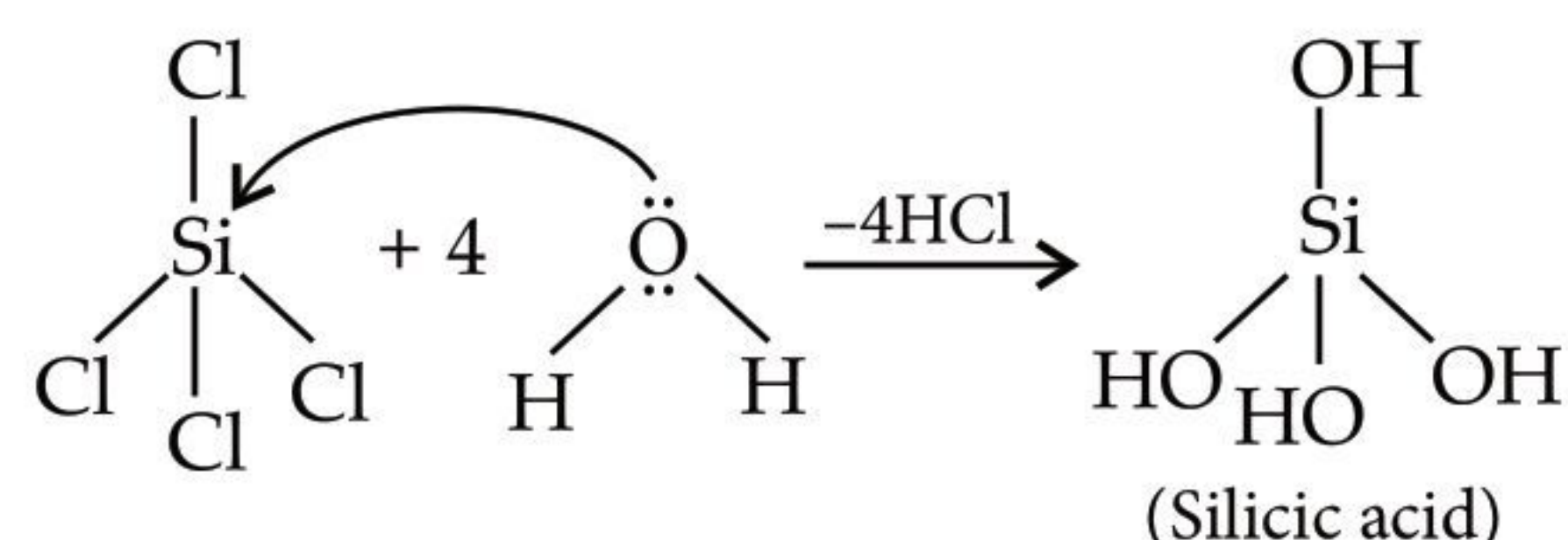
The enthalpy and entropy change for the reaction,

$$\text{Br}_{2(l)} + \text{Cl}_{2(g)} \longrightarrow 2\text{BrCl}_{(g)}$$
 are 30 kJ mol^{-1} and $105 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. What is the temperature at which the reaction will be in equilibrium?

SOLUTIONS

1. (i) CCl_4 is not hydrolysed by water because carbon atom cannot accommodate lone pair of electrons from oxygen atom of water due to absence of d -orbital. SiCl_4

can be hydrolysed to give Si(OH)_4 due to presence of d -orbitals.



(ii) Carbon-carbon bond dissociation energy is higher than that of silicon-silicon bond dissociation energy therefore, carbon has a strong tendency for catenation as compared to silicon.

2. Given : $\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$, $\Delta H = -393.5 \text{ kJ/mol}$
 \Rightarrow Heat released on formation of 44 g $\text{CO}_2 = -393.5 \text{ kJ}$
 \therefore Heat released on formation of 35.2 g CO_2

$$= \frac{-393.5}{44} \times 35.2 = -314.8 \approx -315 \text{ kJ}$$

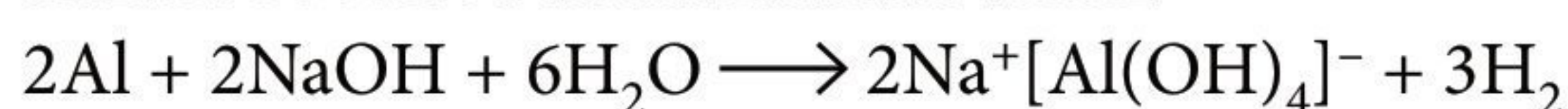
3. For the given reaction : $\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
 $\Delta n_g = 2 - 1 = 1$; $K_p = K_c(RT)^{\Delta n_g}$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{0.14}{(0.083 \times 298)^1} = 5.73 \times 10^{-3} \text{ mol L}^{-1}$$

4. (i) In both the oxides, the oxidation state of metals is +4. In lead, the inert pair effect is maximum hence, its +4 oxidation state is not stable and it readily gets converted to +2 oxidation state. Therefore, PbO_2 acts as a strong oxidising agent. In tin, +4 oxidation state is more stable than +2 oxidation state hence, SnO_2 is a weaker oxidising agent.

(ii) Aluminium turns passive with HNO_3 due to the formation of protective oxide film on its surface. This film prevents the further action of conc. HNO_3 hence, HNO_3 can be stored in aluminium vessel.

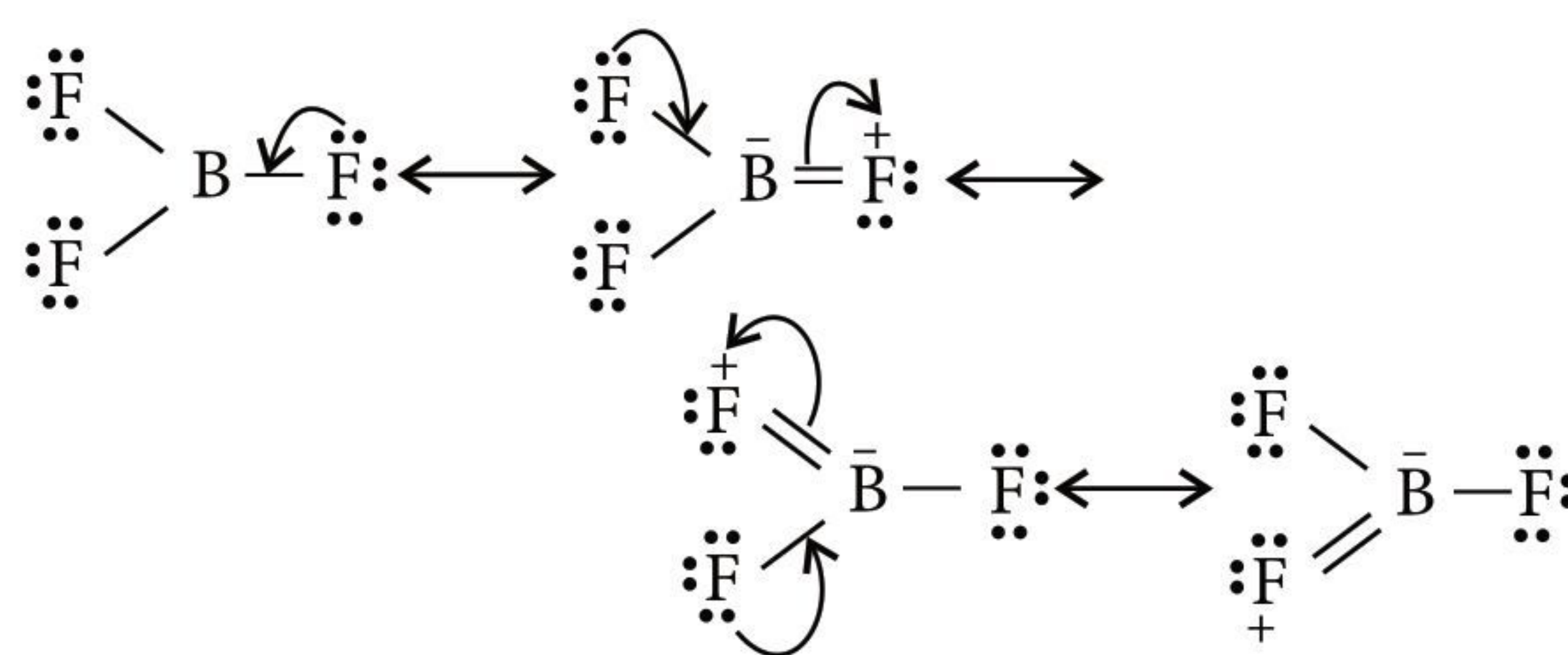
Aluminium dissolves in aqueous NaOH hence, it cannot be stored in aluminium vessel.



(iii) Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make $\text{Al}^{3+}_{(aq)}$ ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidising agent also. Thus Tl^+ is more stable in solution than Tl^{3+} . Aluminium being able to form +3 ions easily, is more electropositive than thallium.

OR

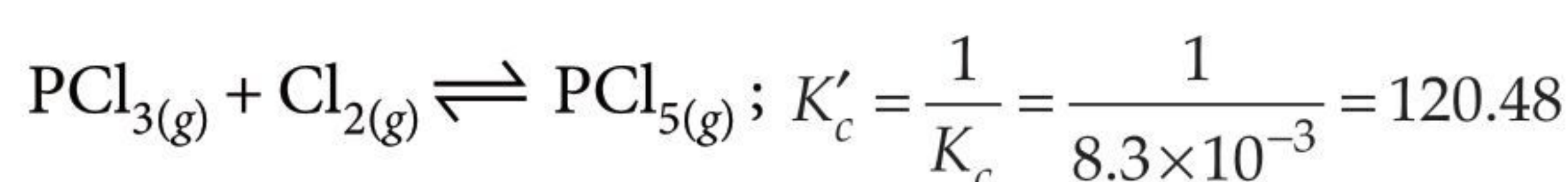
(i) Due to $p\pi$ - $p\pi$ back bonding, the lone pair of electrons of F is donated to the vacant orbital of B-atom. This delocalisation reduces the deficiency of electrons on B thereby increasing the stability of BF_3 molecule.



Due to absence of lone pair of electrons on H-atom, this compensation does not occur in BH_3 . In other words, there is electron deficiency on B atom and hence, to reduce its electron deficiency, BH_3 dimerises to form B_2H_6 .

(ii) B—F bonds in BF_3 have double bond character hence, BF_3 has shorter B—F bond length than BF_4^- .

5. (a) For the reverse reaction :



(b) (i) The value of equilibrium constant is constant for a particular reaction at a particular temperature hence, increase in pressure will have no effect.

(ii) As the reaction is endothermic, the increase in temperature will favour the forward reaction. More PCl_5 will dissociate to form PCl_3 and Cl_2 hence, K_c will increase.

OR



Conc. at $t = 0$: 1 0 0
 Conc. at equilibrium: $1 - S$ S 3 S

$$K_{sp} = [\text{Al}^{3+}] [\text{OH}^-]^3 = (S) (3S)^3 = 27S^4$$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$$

$$S = 1 \times 10^{-3} \text{ mol L}^{-1}$$

Molar mass of $\text{Al(OH)}_3 = 78 \text{ g}$

$$\therefore \text{Solubility of } \text{Al(OH)}_3 \text{ in g L}^{-1} = 1 \times 10^{-3} \times 78$$

$$= 78 \times 10^{-3} = 7.8 \times 10^{-2} \text{ g L}^{-1}$$

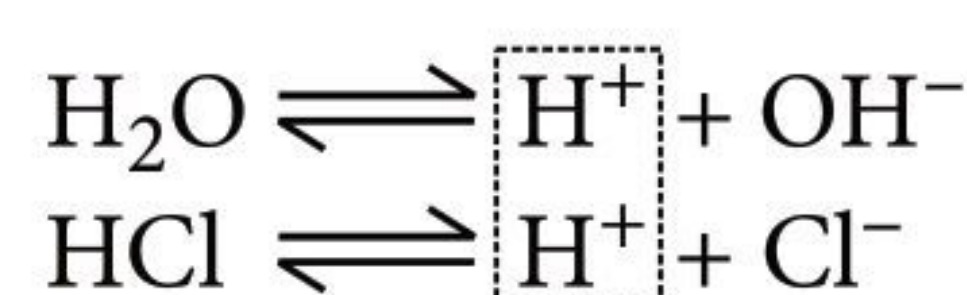
$$\text{pH of the solution : } [\text{OH}^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3 \times 10^{-3})$$

$$\text{pOH} = 3 - \log 3 = 3 - 0.4771 = 2.523$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.523 = 11.477$$

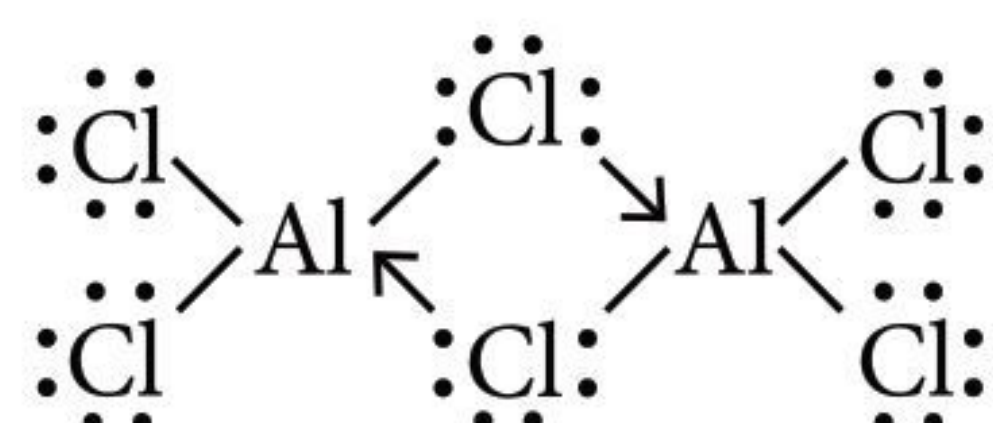
(b) There is no effect of addition of HCl to the ionic product of water due to common ion effect, i.e., $[\text{H}^+]$ concentration increases while $[\text{OH}^-]$ concentration decreases accordingly so that the product $[\text{H}^+][\text{OH}^-]$ remains the same.



6. (i) Diamond has giant three dimensional polymeric structure in which each carbon is sp^3 hybridized and linked to four carbon atoms. This structure makes diamond hardest substance known. On account of small radii of carbon atoms, the various atoms are closely packed in the crystal lattice. Graphite possesses layer structure in which each carbon atom is sp^2 hybridized. There is wide separation between various layers. One layer can slide easily on the other. This makes graphite soft in nature.

(ii) The trihalides of group 13 elements have only six electrons in the valence shell and have a strong tendency to accept a pair of electrons to acquire the nearest inert gas configuration that is why they behave as Lewis acids.

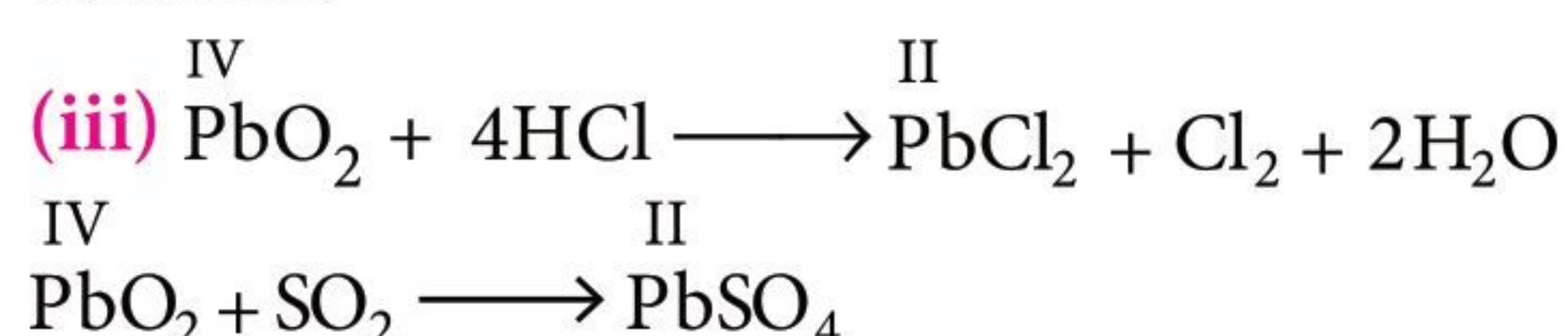
(iii) Aluminium atom in aluminium chloride contains 6 electrons in its outermost orbit. So, it requires 2 more electrons for completion of its octet. This is fulfilled by dimerisation when chlorine atoms donate lone pairs to aluminium atoms as shown below:



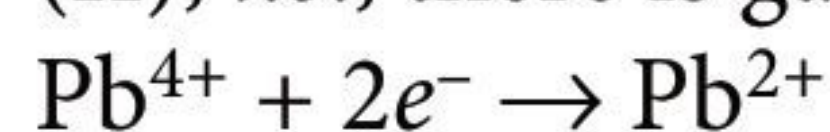
OR

(i) Ionization energy of carbon is quite high due to the small size of the carbon atom. It then decreases for silicon due to the increase in size of silicon atom. Then there is a decrease in ionization energy from Si to Sn. This is because the 'd' electrons which are present in the inner shell of Ge and Sn shield the nuclear charge less effectively than is done by s and p electrons. The outer electrons are held strongly by the nucleus and there is only a small decrease in ionization energy as we move from Si to Sn. In the case of Pb, there is only a marginal increase of atomic radius as we move from Sn to Pb and also there are f-electrons in the inner configuration which shield the nuclear charge less effectively than the 'd' electrons. So, the ionization energy instead of decreasing, shows a marginal increase.

(ii) Graphite has a layered structure in which each C atom is sp^2 hybridised and π -electrons are delocalised to conduct electricity. In diamond, each C atom is sp^3 hybridised and no delocalised or mobile electrons are available.



In above reactions, lead changes from lead (IV) to lead (II), i.e., there is gain of electrons by Pb.



Thus, PbO_2 acts as oxidizing agent as it oxidizes HCl and SO_2 .

$$7. \text{ (a) Here, } Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

As $Q_c \neq K_c$, the reaction is not at equilibrium and $Q_c < K_c$, therefore, the reaction will proceed in the forward direction.

$$\text{(b) } K_{sp} \text{ for } \text{Fe}(\text{OH})_3 = [\text{Fe}^{3+}][\text{OH}^-]^3$$

Precipitation will occur when ionic product, $[\text{Fe}^{3+}][\text{OH}^-]^3$ becomes greater than K_{sp} .

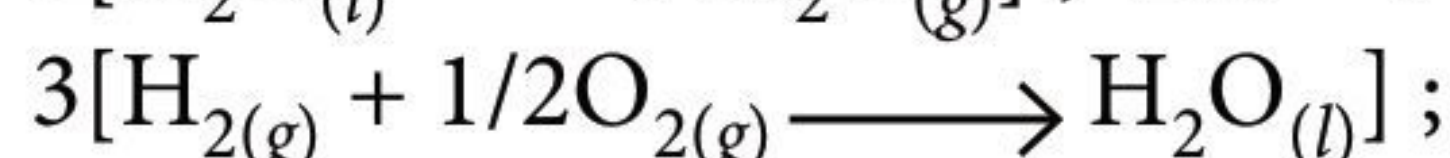
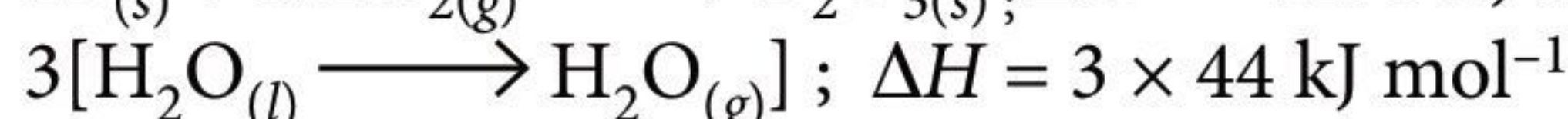
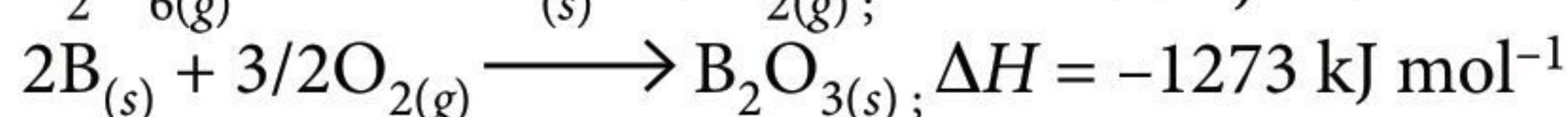
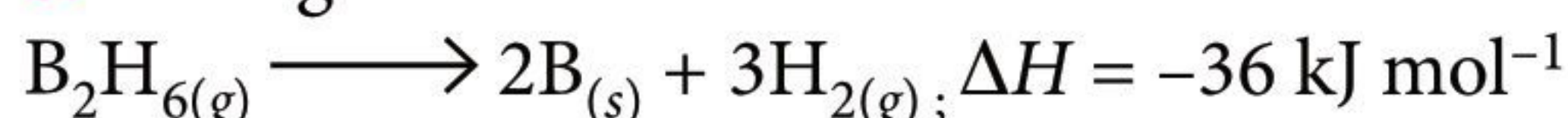
$$[\text{Fe}^{3+}] = [\text{FeCl}_3] = 0.001 \text{ M}$$

$$\therefore [\text{OH}^-]^3 = \frac{K_{sp}}{[\text{Fe}^{3+}]} = \left(\frac{1 \times 10^{-36}}{0.001} \right) = 1 \times 10^{-33}$$

$$\Rightarrow [\text{OH}^-] = (1 \times 10^{-33})^{1/3} = 1 \times 10^{-11} \text{ mol L}^{-1}$$

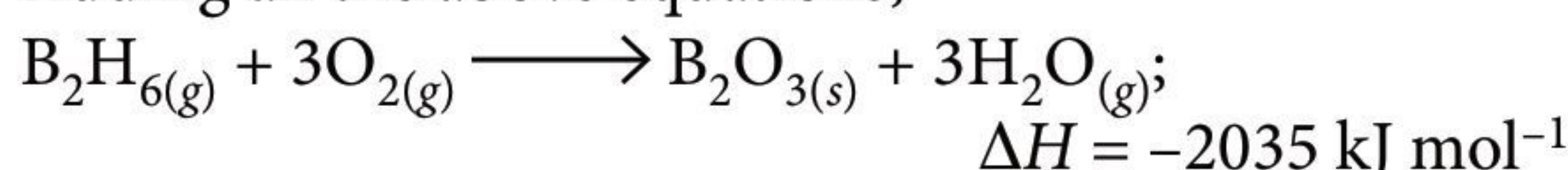
Thus, minimum concentration of OH^- required to start precipitation of $\text{Fe}(\text{OH})_3 = 1 \times 10^{-11} \text{ mol L}^{-1}$.

8. The given reaction can be obtained as follows:

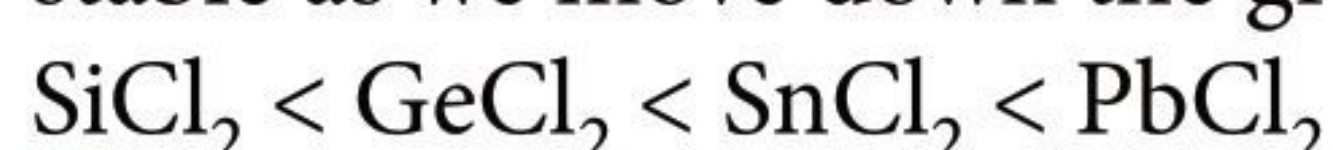


$$\Delta H = -3 \times 286 \text{ kJ mol}^{-1}$$

Adding all the above equations,



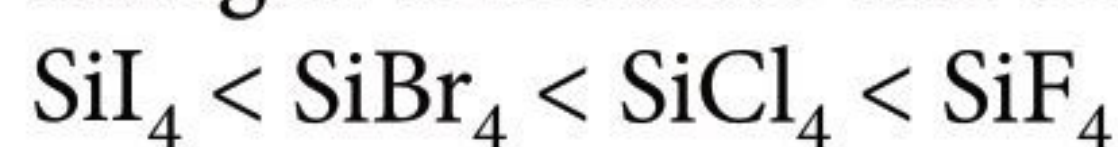
9. (a) The stability of dihalides increases down the group because divalent state becomes more and more stable as we move down the group.



(b) Basicity of oxides increases down the group as metallic character increases.



(c) Si—X bond strength decreases as the size of the halogen increases. The correct order is



$$\begin{aligned} 10. \quad w &= -2.303nRT \log \frac{V_2}{V_1} \\ &= -2.303 \times \frac{10}{40} \times 2 \times 300 \times \log \left(\frac{5}{10} \right) \\ w &= 103.991 \text{ cal} \end{aligned}$$

$$\Delta U = 0, q = \Delta U - w \therefore q = -w = -103.991 \text{ cal}$$

When temperature is constant,

$$P_1V_1 = P_2V_2 \text{ or } PV = \text{constant}$$

$$\Delta H = \Delta U + \Delta(PV) = 0 + 0 = 0.$$

OR

$$T_{\text{system}} = 130^\circ\text{C} = 130 + 273 \text{ K} = 403 \text{ K}$$

$$T_{\text{surr}} = 32^\circ\text{C} = 32 + 273 \text{ K} = 305 \text{ K}$$

$$q_{\text{system}} = -340 \text{ J}, q_{\text{surr}} = +340 \text{ J}$$

$$(i) \Delta S_{\text{system}} = \frac{q_{\text{system}}}{T_{\text{system}}} = \frac{-340 \text{ J}}{403 \text{ K}} = -0.84 \text{ J K}^{-1}$$

$$(ii) \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{+340 \text{ J}}{305 \text{ K}} = +1.11 \text{ J K}^{-1}$$

$$(iii) \Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ = -0.84 + (+1.11) \text{ J K}^{-1} = 0.27 \text{ J K}^{-1}$$

11. When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

(i) When H_2 is added, the rate of forward reaction will increase.

(ii) Removal of CO or addition of CH_3OH will lead to increase in rate of backward reaction.

12. (a) $\Delta G = \Delta H - T\Delta S$

Given, $\Delta H = -\text{ve}$ and $\Delta S = -\text{ve}$

For a reaction to be spontaneous, ΔG should be negative, reaction takes place spontaneously only at lower temperature.

(b) The sign of ΔS for the reaction,

$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$, is +ve as the solid changes into gaseous state.

(c) Whenever a spontaneous process takes place, it is always accompanied by an increase in total entropy of the universe.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

(d) Since $\Delta G = \Delta H - T\Delta S$,

Temperature has minimum value at equilibrium *i.e.*, at $\Delta G = 0 \Rightarrow \Delta H = T\Delta S$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{280 \times 10^3}{140} = 2000 \text{ K}$$

OR

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G = 0$ at equilibrium giving, $T\Delta S = \Delta H$

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{105} = 285.7 \text{ K}$$



Scientist of the Month

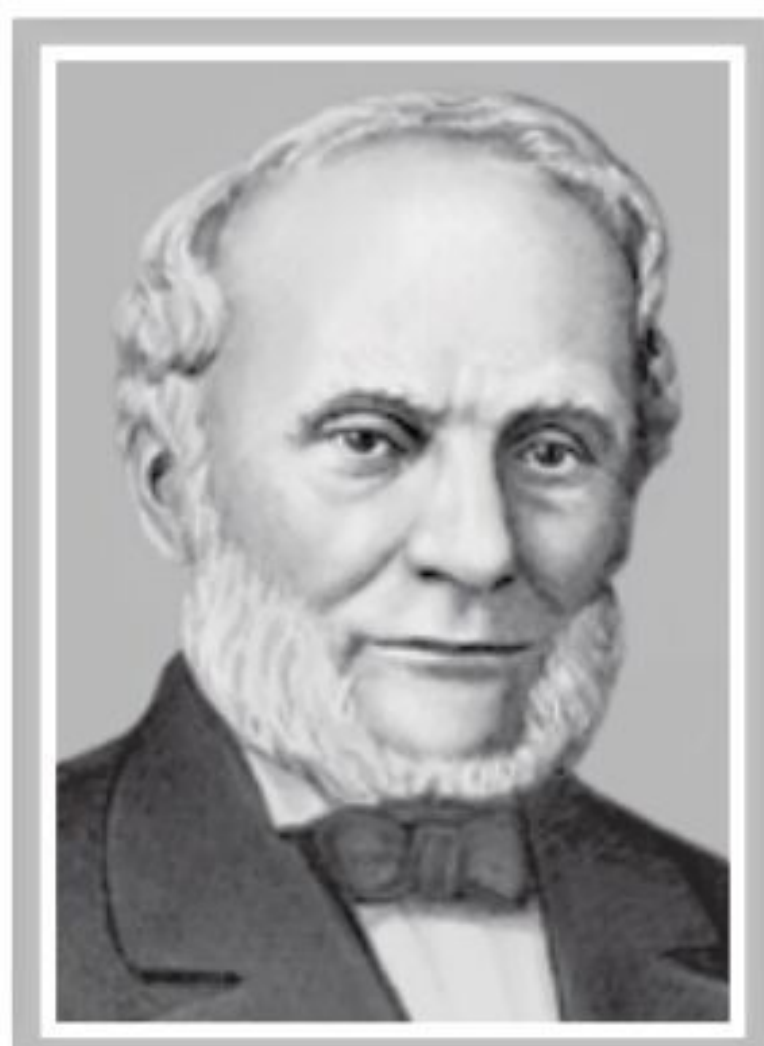
Rudolf Julius Emanuel Clausius

Early Life

- Clausius was born in Köslin (now Koszalin, Poland) in the Province of Pomerania in Prussia. His father was a Protestant pastor and school inspector, and Rudolf studied in the school of his father.

Higher Education

- In 1838, he went to the Gymnasium in Stettin. Clausius graduated from the University of Berlin in 1844 where he had studied mathematics and physics since 1840 with, among others, Gustav Magnus, Peter Gustav Lejeune Dirichlet and Jakob Steiner. He also studied history with Leopold von Ranke. During 1848, he got his doctorate from the University of Halle on optical effects in Earth's atmosphere. In 1850, he became professor of physics at the Royal Artillery and Engineering School in Berlin and Privatdozent at the Berlin University. In 1855, he became professor at the ETH Zürich, the Swiss Federal Institute of Technology in Zürich, where he stayed until 1867. During that year, he moved to Würzburg and two years later, in 1869 to Bonn.



Rudolf Julius Emanuel Clausius
(02 January 1822 - 24 August 1888)

Career and Discoveries

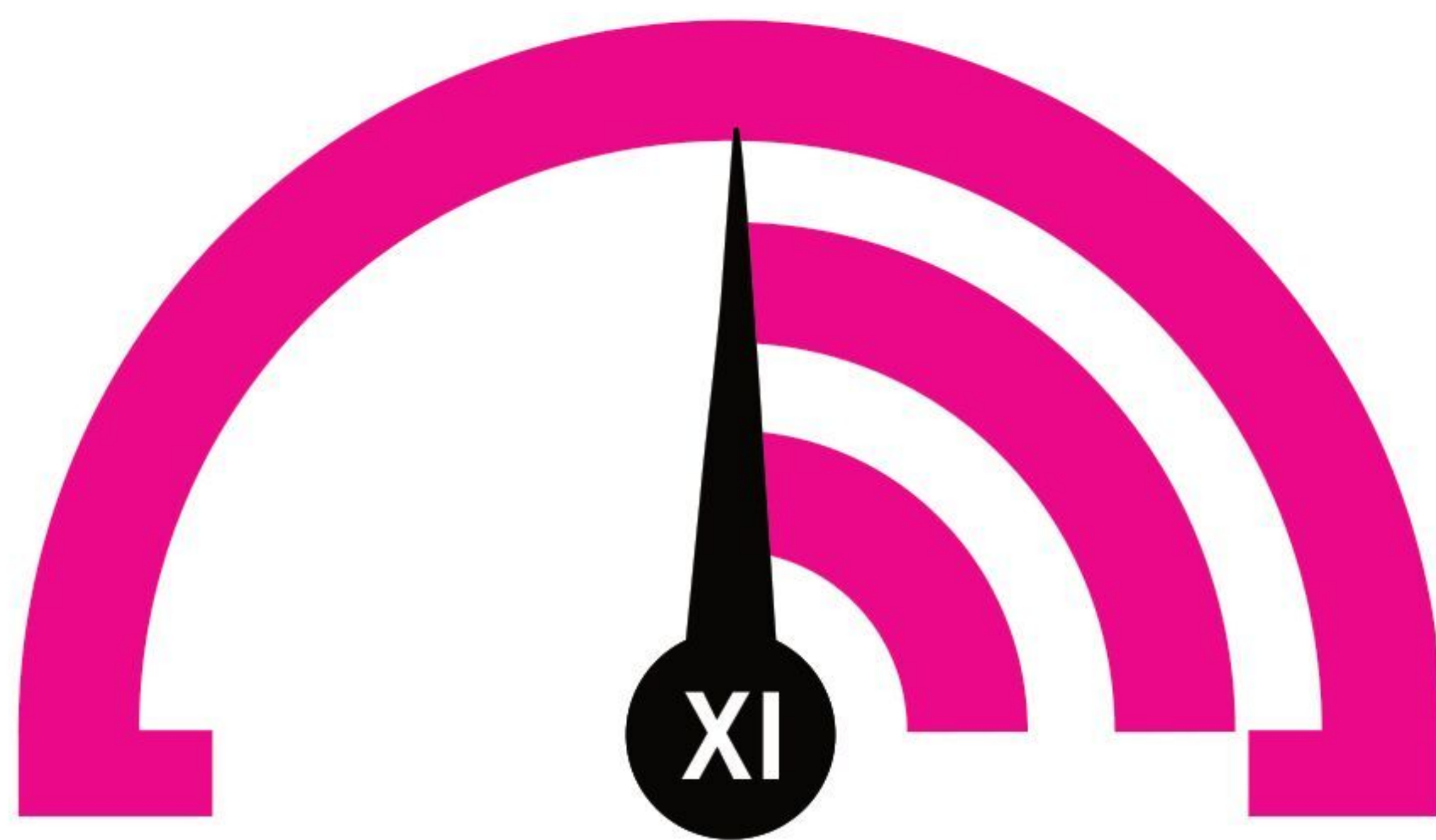
- Clausius' PhD thesis concerning the refraction of light proposed that we see a blue sky during the day and various shades of red at sunrise and sunset (among other phenomena) due to reflection and refraction of light.
- His most famous paper, Ueber die bewegende Kraft der Wärme ("On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom") was published in 1850, and dealt with the mechanical theory of heat. In this paper, he showed that there was a contradiction between Carnot's principle and the concept of conservation of energy. Clausius restated the two laws of thermodynamics to overcome this contradiction (the third law was developed by Walther Nernst, during the years 1906–1912). This paper made him famous among scientists.

- Clausius' most famous statement of thermodynamics second law was published in German in 1854, and in English in 1856. "Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time."
- During 1857, Clausius contributed to the field of kinetic theory after refining August Krönig's very simple gas-kinetic model to include translational, rotational and vibrational molecular motions. In this same work he introduced the concept of 'mean free path' of a particle.
- Clausius deduced the Clausius–Clapeyron relation from thermodynamics. This relation, which is a way of characterizing the phase transition between two states of matter such as solid and liquid, had originally been developed in 1834 by Émile Clapeyron.
- In 1865, Clausius gave the first mathematical version of the concept of entropy, and also gave it its name. Clausius chose the word because the meaning from the Greek is "content transformative" or "transformation content". He used the now abandoned unit 'Clausius' (symbol: Cl) for entropy.
- 1 Clausius (Cl) = 1 calorie/degree Celsius (cal/°C) = 4.1868 joules per kelvin (J/K)

Honours and Awards

- Honorary Membership of the Institution of Engineers and Shipbuilders in Scotland in 1859.
- Fellow of the Royal Society of London in 1868 and received its Copley Medal in 1879.
- Member of the Royal Swedish Academy of Sciences in 1878.
- Huygens Medal in 1870.
- Foreign Member of the Accademia Nazionale dei Lincei in Rome in 1880.
- Member of the German Academy of Sciences Leopoldina in 1880.
- Poncelet Prize in 1883.
- Honorary doctorate from the University of Würzburg in 1882.
- Foreign Member of the Royal Netherlands Academy of Arts and Sciences in 1886.
- The lunar crater Clausius named in his honor.
- A memorial in his home town of Koszalin in 2009.

MONTHLY TEST DRIVE



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks : 120

States of Matter | Thermodynamics

Time Taken : 60 Min.

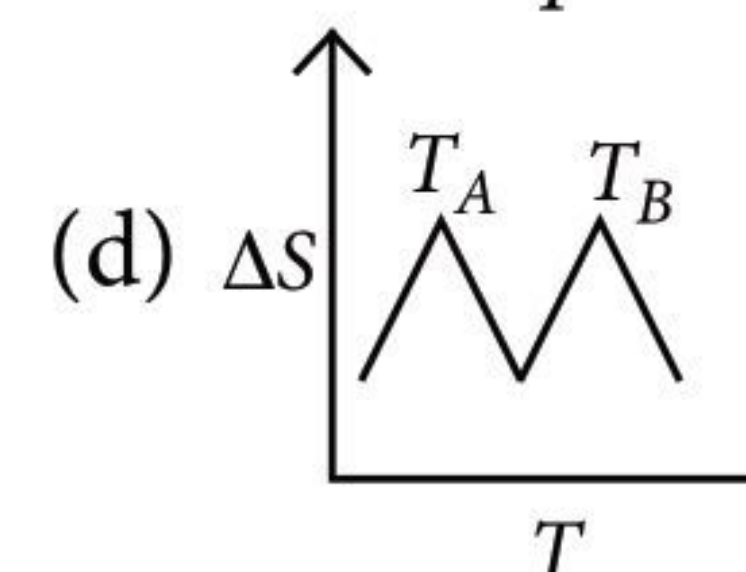
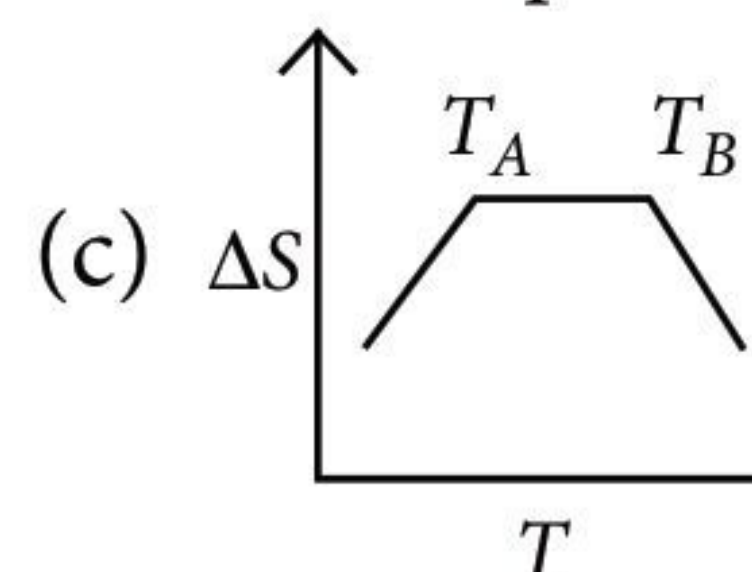
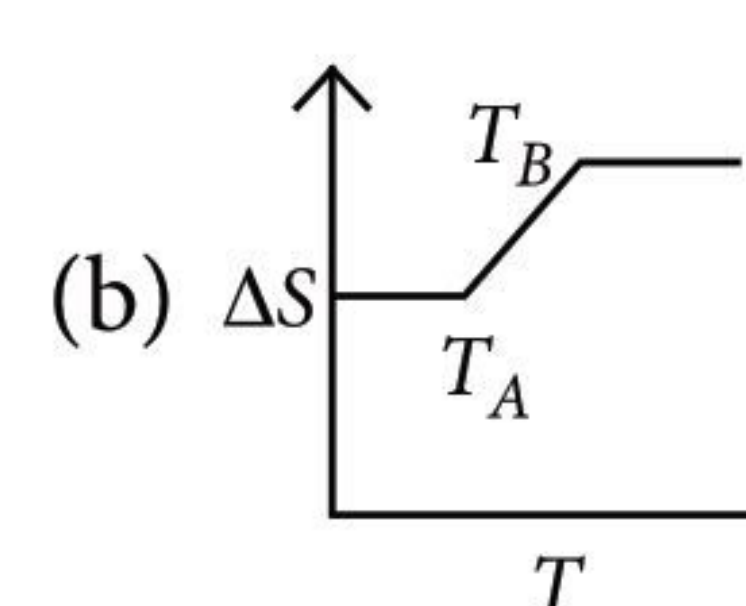
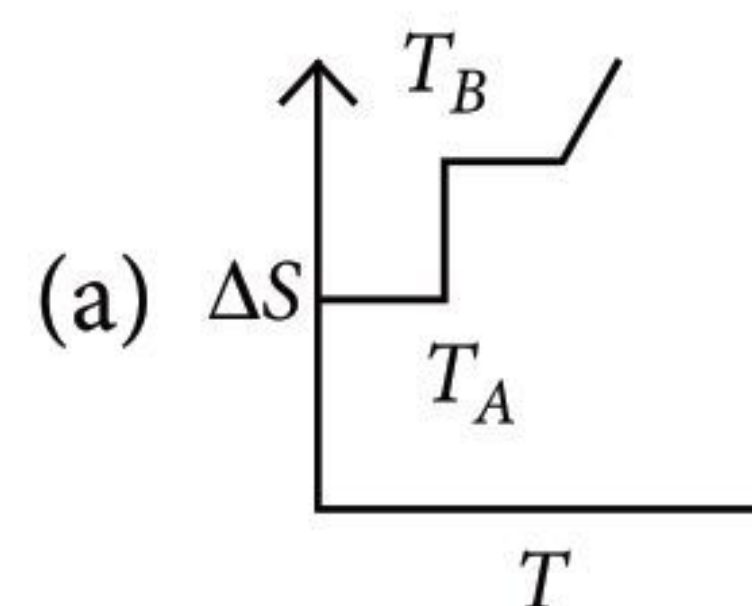
NEET

Only One Option Correct Type

- According to Charles' law,
(a) $(dV/dT)_P = K$ (b) $(dV/dT)_P = -K$
(c) $(dV/dT)_P = -K/T$ (d) none of these.
- The internal energy change when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path. What would be the net change in internal energy?
(a) 40 kJ (b) > 40 kJ
(c) < 40 kJ (d) zero
- The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as :
 $S_{2(g)} + 2O_{2(g)} \rightarrow 2SO_{2(g)} ; \Delta G = -544 \text{ kJ}$
 $2Zn_{(s)} + S_{2(g)} \rightarrow 2ZnS_{(s)} ; \Delta G = -293 \text{ kJ}$
 $2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)} ; \Delta G = -480 \text{ kJ}$
 The ΔG for the reaction
 $2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$ will be
 (a) -731 kJ (b) -773 kJ
 (c) -229 kJ (d) -357 kJ
- Which of the following statements is correct if the intermolecular forces in liquids A, B and C are in the order $A < B < C$?
 (a) B evaporates more readily than A.
 (b) B evaporates less readily than C.
 (c) A and B evaporate at the same rate.
 (d) A evaporates more readily than C.
- One gram atom of graphite and one gram atom of diamond were separately burnt to carbon dioxide.

The amount of heat liberated were 393.5 kJ and 395.4 kJ respectively. It shows that

- graphite has greater affinity for oxygen
 - diamond has greater affinity for oxygen
 - graphite is stable than diamond
 - diamond is stable than graphite.
- A certain gas diffuses from two different vessels A and B. The vessel A has a circular orifice while vessel B has square orifice of length equal to the radius of the orifice of vessel A. The ratio of the rates of diffusion of the gas from vessel A to vessel B, assuming same temperature and pressure is
(a) π (b) 7:22 (c) 1:1 (d) 2:1
 - If the pressure at the triple point of a substance is greater than 1 atm, we expect
 (a) the boiling point of the liquid to be lower than triple point temperature
 (b) that the substance cannot exist as a liquid
 (c) the solid sublimates without melting
 (d) the melting point of the solid to be a higher temperature than the triple point temperature.
 - If for a given substance (pure), melting point is T_B and freezing point is T_A , then correct graph between entropy change and temperature is



9. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then

(a) ΔH is -ve, ΔS is +ve
 (b) ΔH and ΔS both are +ve
 (c) ΔH and ΔS both are -ve
 (d) ΔH is +ve, ΔS is -ve.

10. Which of the following expressions between the van der Waals' constant, ' b ' and the radius ' r ' of spherical molecule is correct?

(a) $b = \left[\frac{4}{3} \pi r^3 \right] N_A$ (b) $b = \left[\frac{4}{3} \pi r^3 \right]$
 (c) $b = 2 \left[\frac{4}{3} \pi r^3 \right] N_A$ (d) $b = 4 \left[\frac{4}{3} \pi r^3 \right] N_A$

11. A vessel of 50 L capacity contains 0.5 mol of O_2 at $27^\circ C$ under a pressure of 2 atm. If half of the molecules of O_2 are removed from the vessel then *rms* speed of O_2 molecules will

(a) increase (b) decrease
 (c) not change (d) first increase then decrease.

12. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is equal to 1 atm lit^{-1} . What is molar heat capacity of gas?

(a) $4R/2$ (b) $3R/2$ (c) $5R/2$ (d) zero

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 (c) If assertion is true but reason is false.
 (d) If both assertion and reason are false.

13. **Assertion :** The heat absorbed during isothermal expansion of an ideal gas against vacuum is zero.

Reason : The volume occupied by the molecules of an ideal gas is zero.

14. **Assertion :** During evaporation of liquid the temperature of the liquid remains unaffected.

Reason : Kinetic energy of the molecules is directly proportional to absolute temperature.

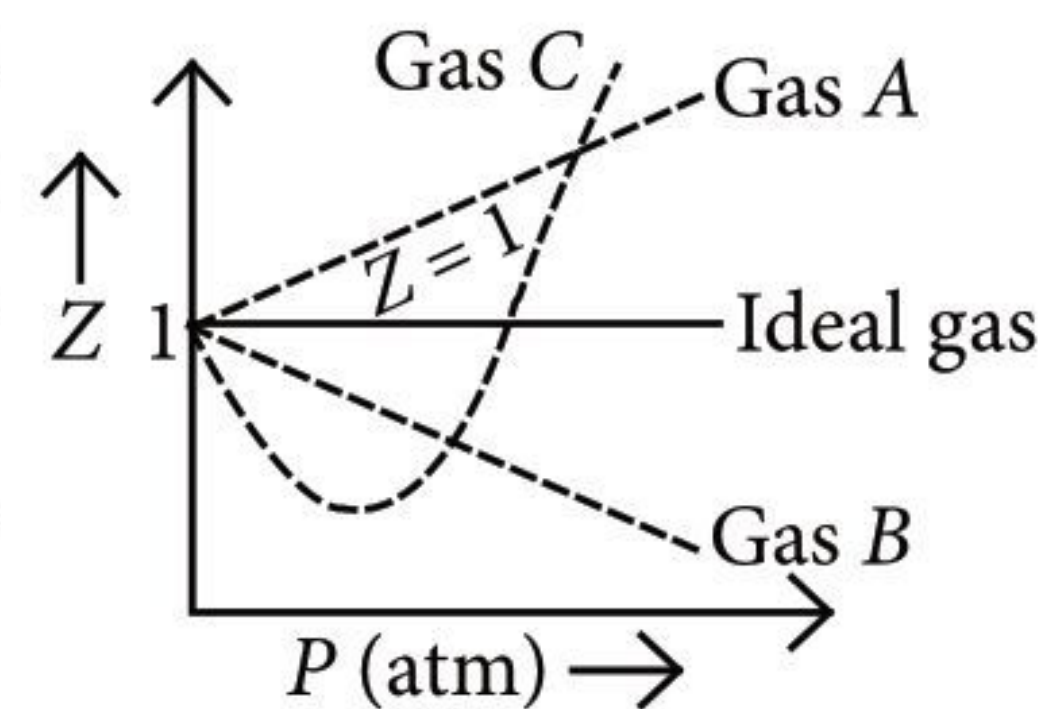
15. **Assertion :** The heat of neutralisation of $HNO_3 + NH_4OH$ is -51.66 kJ .

Reason : The heat of neutralisation of $NH_4OH + CH_3COOH$ is -55.78 kJ .

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. The given graph represents the variation of compressibility factor $Z = \frac{PV}{nRT}$ versus P , for three real gases A, B and C.



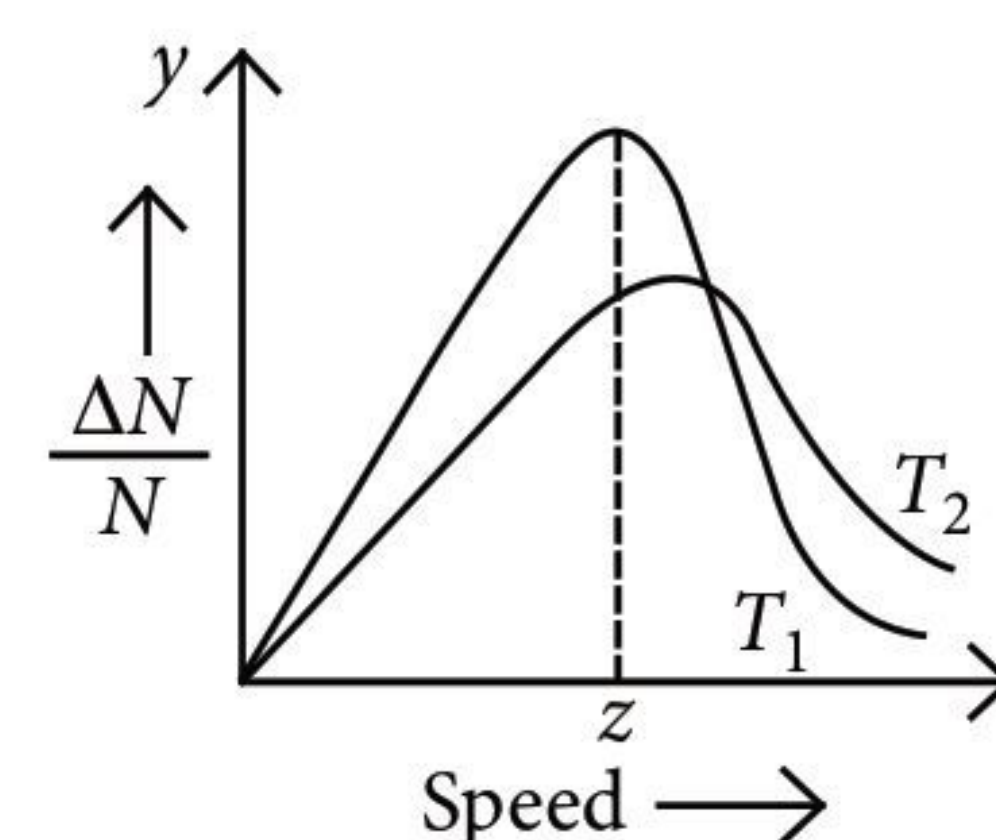
Identify the incorrect statement.

- (a) For the gas A, $a = 0$ and its dependence on P is linear at all pressures.
 (b) For the gas B, $b = 0$ and its dependence on P is linear at all pressure.
 (c) For the gas C, which is a typical real gas for which neither a nor $b = 0$. By knowing the minima and point of the intersection, with $Z = 1$, a and b can be calculated.
 (d) At high pressure, the slope is positive for all real gases.

17. One mole of a non-ideal gas undergoes a change of state ($2.0 \text{ atm}, 3.0 \text{ L}, 95 \text{ K}$) \rightarrow ($4.0 \text{ atm}, 5.0 \text{ L}, 245 \text{ K}$) with a change in internal energy, $\Delta U = 30.0 \text{ L atm}$. The change in enthalpy (ΔH) of the process (in L atm) is

(a) 40.0 (b) 42.3
 (c) 44.0 (d) not defined because pressure is not constant.

18. Consider the given curve, the correct relationship between T_1 and T_2 is



(a) $T_1 < T_2$
 (b) $T_2 > T_1$
 (c) $T_1 = T_2$
 (d) can't be predicted.

19. For a van der Waal' gas at critical point, the volume of gas is equal to

(a) 4 times of actual volume
 (b) 8 times of actual volume
 (c) 12 times of actual volume
 (d) 16 times of actual volume.

More than One Options Correct Type

20. In the reaction: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$; $\Delta H = -x \text{ kJ}$.

(a) $x \text{ kJ}$ is the heat of reaction
 (b) $x \text{ kJ}$ is the heat of formation of H_2O
 (c) $x \text{ kJ}$ is the heat of combustion of H_2
 (d) $(x/2) \text{ kJ}$ is the heat of formation of H_2O

21. Which of the following expressions represent Boyle's law?

- (a) $PV = \text{constant}$ (b) $V \propto \frac{1}{P}$
 (c) $V_1 T_2 = V_2 T_1$ (d) $P_1 V_1 = P_2 V_2$

22. Which of the following statements are correct?
 (a) Helium diffuses at a rate 8.65 times as much as CO does.
 (b) Helium diffuses at a rate 2.65 times as fast as CO does.
 (c) Helium diffuses at a rate of 4 times faster than CO_2 .
 (d) Helium diffuses at a rate of 4 times as fast as SO_2 does.
23. The standard enthalpies of formation of $\text{CO}_{2(g)}$ and $\text{HCOOH}_{(l)}$ are $-393.7 \text{ kJ mol}^{-1}$ and $-409.2 \text{ kJ mol}^{-1}$ respectively. Which of the following statements are correct?
 (a) $-393.7 \text{ kJ mol}^{-1}$ is the enthalpy change for the reaction, $\text{C}_{(s)} + \text{O}_{2(g)} \longrightarrow \text{CO}_{2(g)}$
 (b) The enthalpy change for the reaction, $\text{CO}_{2(g)} + \text{H}_{2(g)} \longrightarrow \text{HCOOH}_{(l)}$ would be $-15.5 \text{ kJ mol}^{-1}$
 (c) The enthalpy change for the reaction, $\text{H}_2\text{O} + \text{CO} \longrightarrow \text{HCOOH}$, is -409 kJ mol^{-1}
 (d) The enthalpy change for the reaction, $\text{H}_{2(g)} + \text{CO}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)} + \text{CO}_{(g)}$, is $-409.2 \text{ kJ mol}^{-1}$

Integer / Numerical Value Type

24. When 2 g of a gaseous substance A is introduced into an initially evacuated flask kept at 25°C , the pressure is found to be 101.325 kPa. The flask is evacuated and 3 g of B(g) is introduced. This time pressure was found to be 50.662 kPa at 25°C . How much times the molecule B is heavier than molecule A.
25. For a reaction, $M_2\text{O}_{(s)} \longrightarrow 2M_{(s)} + \frac{1}{2}\text{O}_{2(g)}$
 $\Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm. Calculate upto what temperature (in K), the reaction would not be spontaneous.
26. 2 moles of a perfect gas are expanded isothermally and reversibly from 5 atm to 1 atm at 27°C . Calculate the expansion work done (in kJ) during the process.

Comprehension Type

A volume of 95 mL N_2O at 27°C is collected in a graduated tube over mercury, the level of Hg inside the tube being 60 mm above the outside mercury level when barometer reads 750 mm.

27. The volume of same mass at STP is
 (a) 0.078 mL (b) 0.064 mL
 (c) 78.48 mL (d) 64.56 mL
28. What volume would the same mass of gas occupy at 40°C when the barometer pressure being 745 mm and the level of Hg inside the tube 25 mm below the outside level?
 (a) 8 mL (b) 88.8 mL (c) 56 mL (d) 5.6 mL

Matrix Match Type

29. Match the column I with column II and select the correct option.

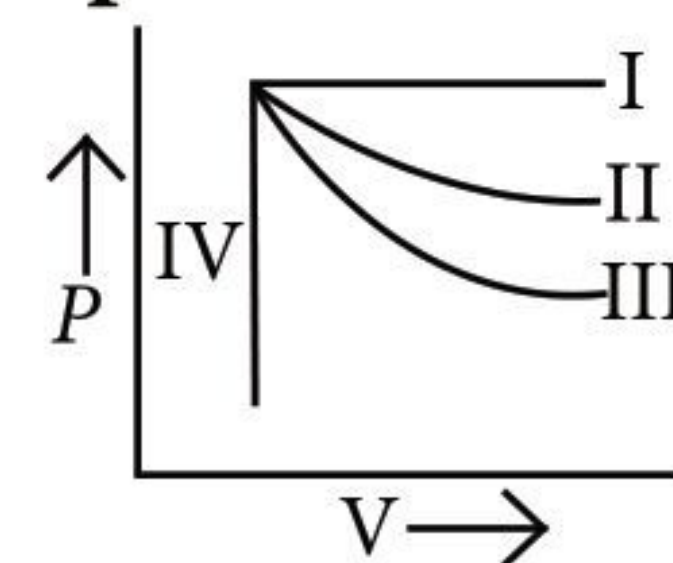
Column I	Column II
(A) Between phosphine molecules	(P) London forces
(B) Between <i>neo</i> -pentane molecules	(Q) Dipole-induced dipole interactions
(C) Between He and HCl molecules	(R) Dipole-dipole interactions
(D) Between NH_3 molecules	(S) Hydrogen bonding

The correct match of the contents in column I with those in column II is

- (a) A-P, B-R, C-S, D-Q (b) A-R, B-P, C-Q, D-S
 (c) A-Q, B-R, C-P, D-S (d) A-S, B-P, C-Q, D-R
30. Which of the following is correct match as far as the thermodynamic processes are involved?

List I Curve	List II Thermodynamic process
A. I	1. Adiabatic
B. II	2. Isochoric
C. III	3. Isobaric
D. IV	4. Isothermal

- (a) A-1, B-2, C-3, D-4 (b) A-3, B-4, C-1, D-2
 (c) A-2, B-1, C-4, D-3 (d) A-3, B-4, C-2, D-1



Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted
 No. of questions correct
 Marks scored in percentage

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

GET SET GO for JEE



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- The density of solid argon is 1.65 g per cc at 25°C. If the argon atom is assumed to be a sphere of radius 1.54×10^{-8} cm, what percent of solid argon is apparently empty space? (Atomic mass of Ar is 40 g mol^{-1} .)
(a) 16.5% (b) 38% (c) 50% (d) 62%
- For a binary solution exhibiting negative deviation from Raoult's law, which of the following set of conditions is true?
(a) $\Delta_{\text{mix}}H < \Delta_{\text{mix}}H_{(\text{ideal})}$; $\Delta_{\text{mix}}S < \Delta_{\text{mix}}S_{(\text{ideal})}$
 $\Delta_{\text{mix}}G < 0$; $p_A < p_{A(\text{ideal})}$
(b) $\Delta_{\text{mix}}H < \Delta_{\text{mix}}H_{(\text{ideal})}$; $\Delta_{\text{mix}}S < \Delta_{\text{mix}}S_{(\text{ideal})}$
 $\Delta_{\text{mix}}G > 0$; $p_A > p_{A(\text{ideal})}$
(c) $\Delta_{\text{mix}}H > \Delta_{\text{mix}}H_{(\text{ideal})}$; $\Delta_{\text{mix}}S < \Delta_{\text{mix}}S_{(\text{ideal})}$
 $\Delta_{\text{mix}}G < 0$; $p_A < p_{A(\text{ideal})}$
(d) $\Delta_{\text{mix}}H < \Delta_{\text{mix}}H_{(\text{ideal})}$; $\Delta_{\text{mix}}S > \Delta_{\text{mix}}S_{(\text{ideal})}$
 $\Delta_{\text{mix}}G < 0$; $p_A > p_{A(\text{ideal})}$
- Consider the following electrodes :
 $P = \text{Zn}^{2+} (0.0001 \text{ M})/\text{Zn}$; $Q = \text{Zn}^{2+} (0.1 \text{ M})/\text{Zn}$
 $R = \text{Zn}^{2+} (0.01 \text{ M})/\text{Zn}$; $S = \text{Zn}^{2+} (0.001 \text{ M})/\text{Zn}$
If $E^\circ_{\text{Zn}/\text{Zn}^{2+}} = -0.76 \text{ V}$, then electrode potentials of the above electrode in volts are in the order
(a) $P > S > R > Q$ (b) $S > R > Q > P$
(c) $Q > R > S > P$ (d) $P > Q > R > S$
- The half-lives of two samples are 0.1 s and 0.8 s and their respective initial concentrations are 400 mol L^{-1} and 50 mol L^{-1} . The order of the reaction is
(a) 0 (b) 2 (c) 1 (d) 4
- Zeta potential is
(a) potential required to bring about coagulation of a colloidal sol
(b) potential required to give the particle a speed of 1 cm s^{-1}
(c) potential difference between fixed charged layer and the diffused layer having opposite charges
(d) potential energy of the colloidal particles.
- According to the following diagram, A reduces BO_2 when the temperature is

T (°C)	ΔG° (kJ mol ⁻¹) for $A + O_2 \rightarrow AO_2$	ΔG° (kJ mol ⁻¹) for $B + O_2 \rightarrow BO_2$
0	-1100	-1150
200	-1080	-1130
400	-1060	-1110
600	-1040	-1090
800	-1020	-1070
1000	-1000	-1050
1200	-980	-1030
1400	-960	-1010
1600	-940	-990

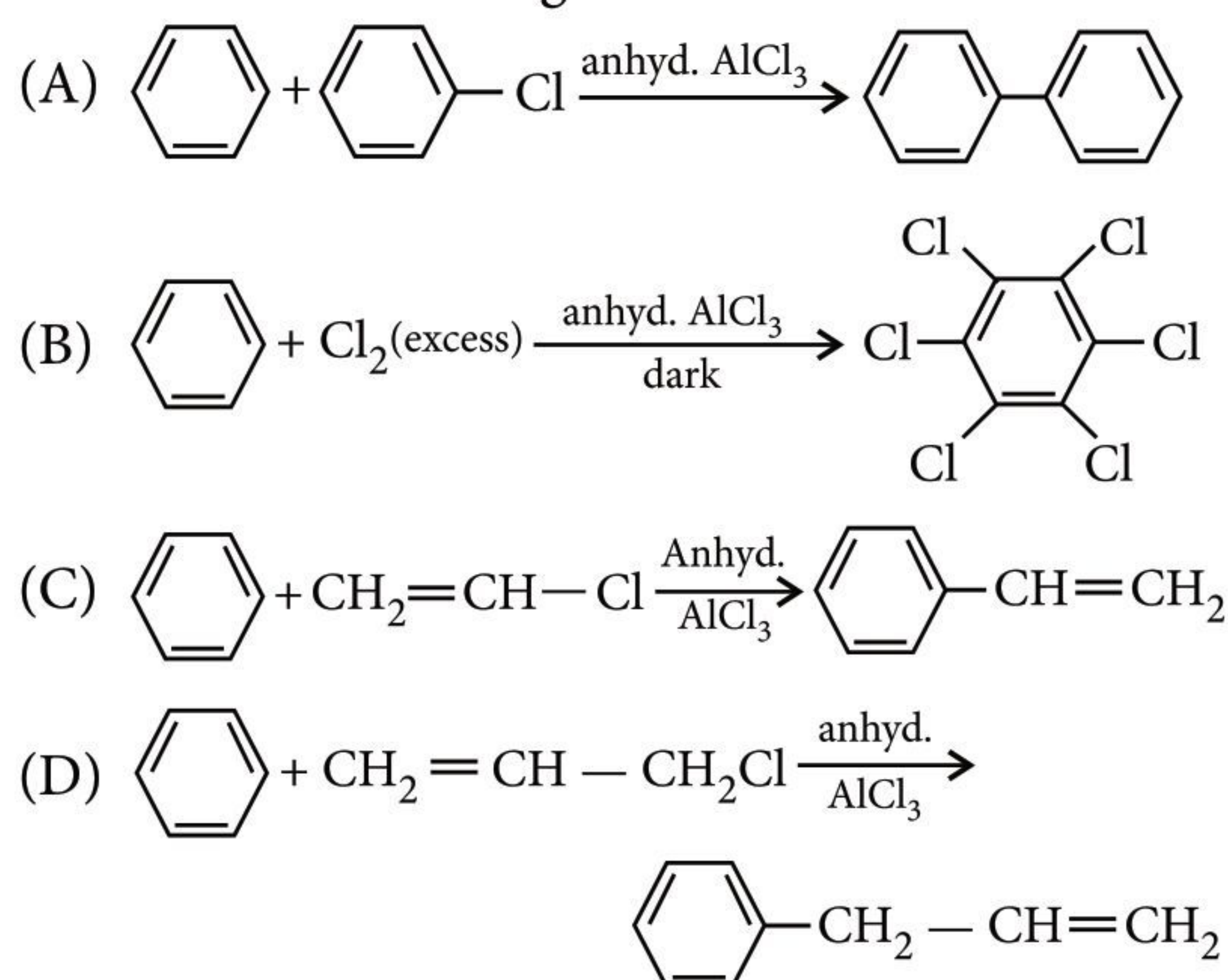
(a) $> 1200^\circ\text{C}$ but $< 1400^\circ\text{C}$
(b) $> 1400^\circ\text{C}$
(c) $< 1200^\circ\text{C}$ (d) $< 1400^\circ\text{C}$

7. Number of Cl=O bonds in chlorous acid, chloric acid and perchloric acid respectively are
 (a) 4, 1 and 0 (b) 3, 1 and 1
 (c) 1, 1 and 3 (d) 1, 2 and 3

8. How many peroxy linkages are present in CrO_5 ?
 (a) 1 (b) 2 (c) 3 (d) 4

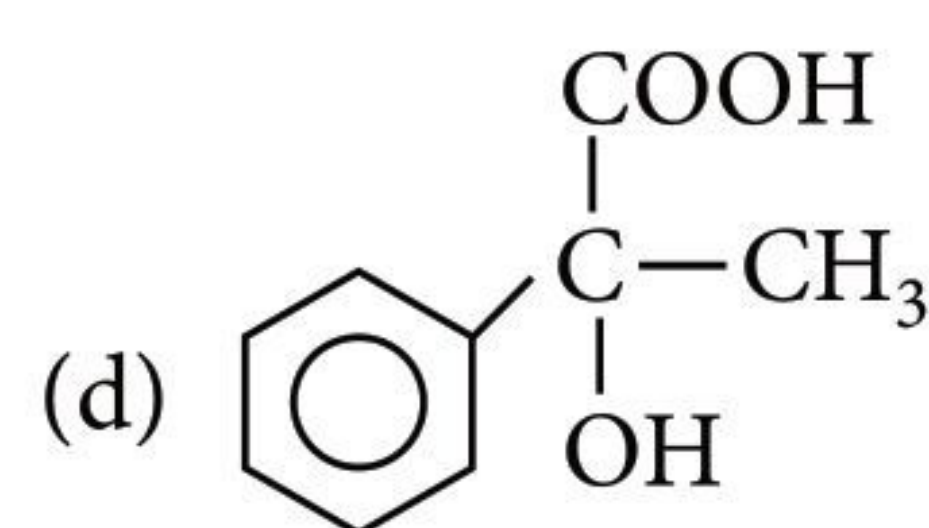
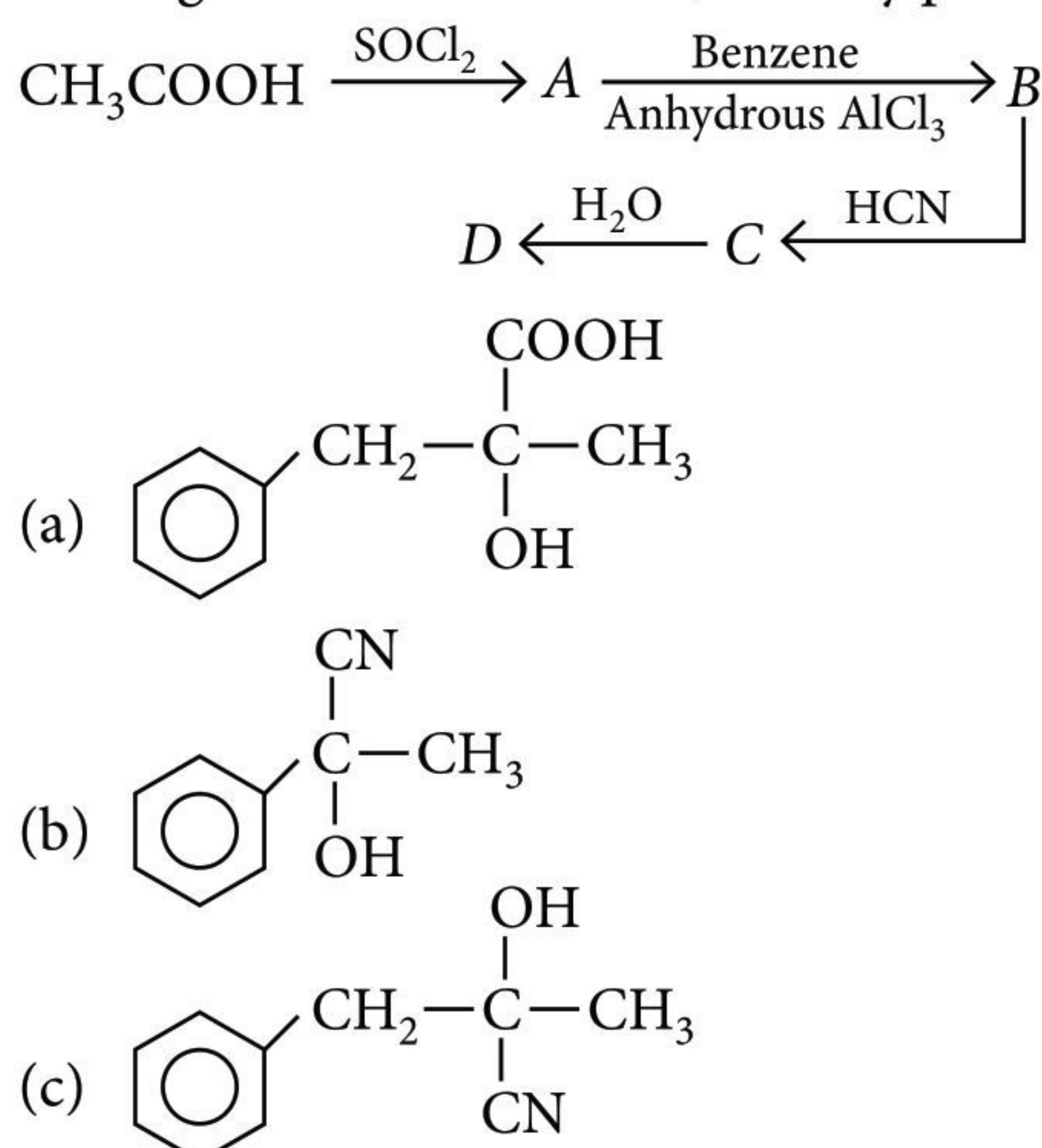
9. The octahedral complexes of a metal ion M^{3+} with four monodentate ligands L_1 , L_2 , L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is
 (a) $L_1 < L_2 < L_4 < L_3$ (b) $L_4 < L_3 < L_2 < L_1$
 (c) $L_1 < L_3 < L_2 < L_4$ (d) $L_3 < L_2 < L_4 < L_1$

10. Consider the following reactions.

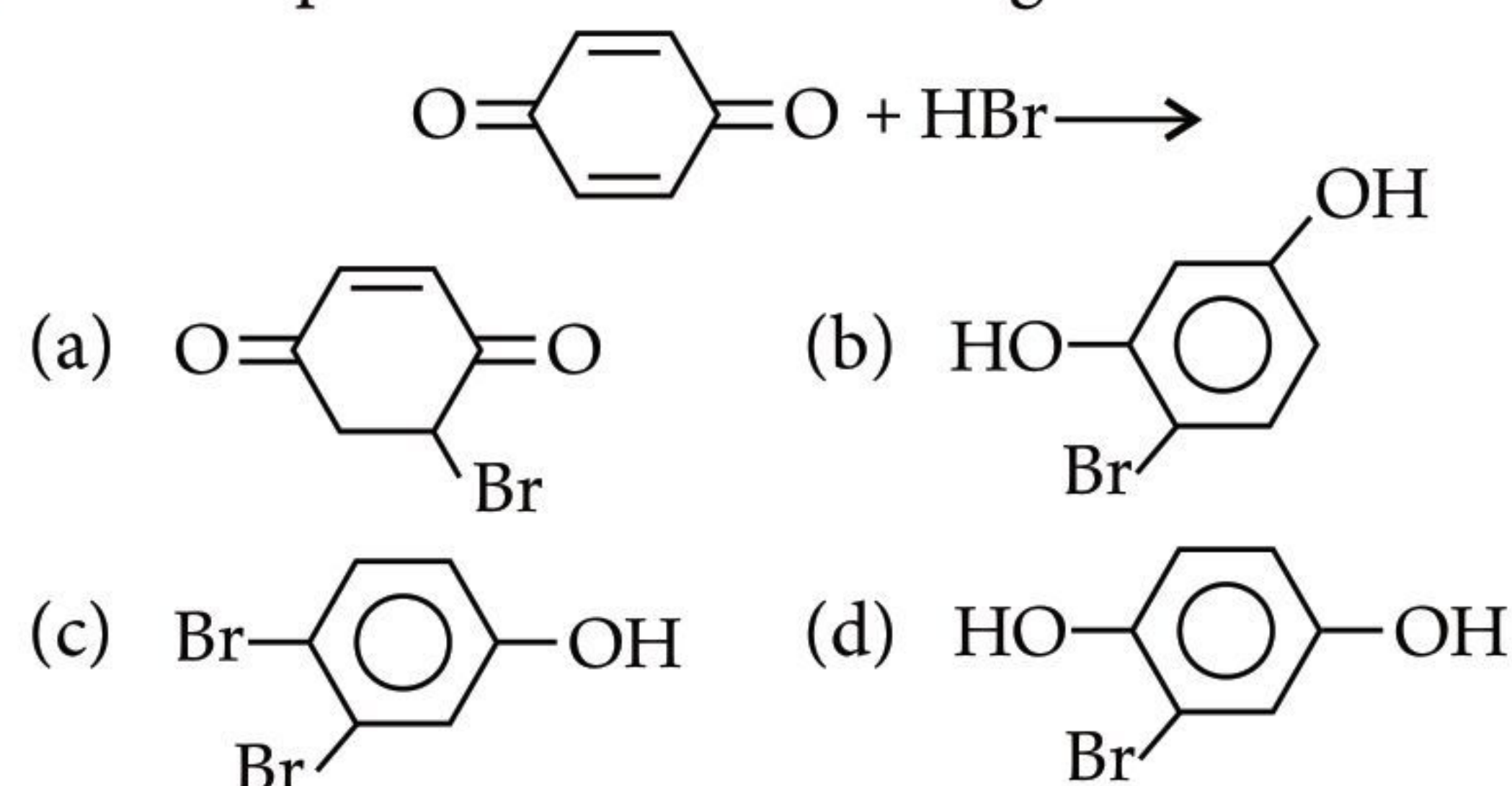


Which of these reactions are possible?

- (a) (A) and (B) (b) (B) and (D)
 (c) (A) and (D) (d) (B), (C) and (D)
11. In the given set of reactions, identify product D.



12. The end product of the following reaction is



NUMERICAL PROBLEMS

13. 36.4 g of 1,1,2,2-tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal AgNO_3 . What is the weight of precipitate (in g) obtained?
14. Among the following polymers, total number of condensation copolymers is _____.
 Nylon-6,6, Buna-S, PVC, Dacron, Bakelite, Natural rubber, Buna-N, PHBV, Glyptal
15. The average molecular mass of starch given that an aqueous solution of 10.0 g/L of starch has an osmotic pressure 5.0×10^{-3} atm at 25°C is _____.

SOLUTIONS

1. (d): Volume of one molecule $= \frac{4}{3}\pi r^3$
 $= \frac{4}{3}\pi (1.54 \times 10^{-8})^3 \text{ cm}^3 = 1.53 \times 10^{-23} \text{ cm}^3$

Volume of all molecules in 1.65 g of Ar

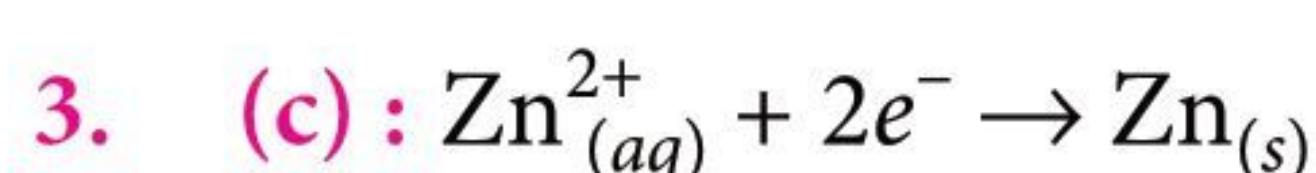
$$= \frac{1.65}{40} \times N_A \times 1.53 \times 10^{-23} = 0.380 \text{ cm}^3$$

Volume of solid Ar containing 1.65 g of Ar = 1 cm^3

$$\therefore \text{Empty space} = 1 - 0.380 = 0.620$$

$$\therefore \text{Percent of empty space} = 62\%$$

2. (a): A mixture of acetone and chloroform shows negative deviation from Raoult's law.
 $\Delta_{\text{mix}}H = -\text{ve}$ (due to formation of H-bond)
 $\Delta_{\text{mix}}S = -\text{ve}$ (due to association of molecules)
 $\Delta_{\text{mix}}G = -\text{ve}$ (as the mixing of components to form solution is spontaneous)
 $p_A < p_{A(\text{ideal})}$ (stronger attraction leads to decrease in escaping tendency.)



$$E_{\text{red}} = E_{\text{red}}^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$E_{\text{red}} = -0.76 + \frac{0.059}{2} \log [\text{Zn}^{2+}] \text{ as } [\text{Zn}^{2+}] \uparrow, E_{\text{red}} \uparrow$$

So, the correct order is $Q > R > S > P$.

4. (b) : We know that, $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{a_2}{a_1} \right]^{n-1}$

where, n = order of the reaction

Given, $(t_{1/2})_1 = 0.1 \text{ s}$, $a_1 = 400 \text{ mol L}^{-1}$

$(t_{1/2})_2 = 0.8 \text{ s}$, $a_2 = 50 \text{ mol L}^{-1}$

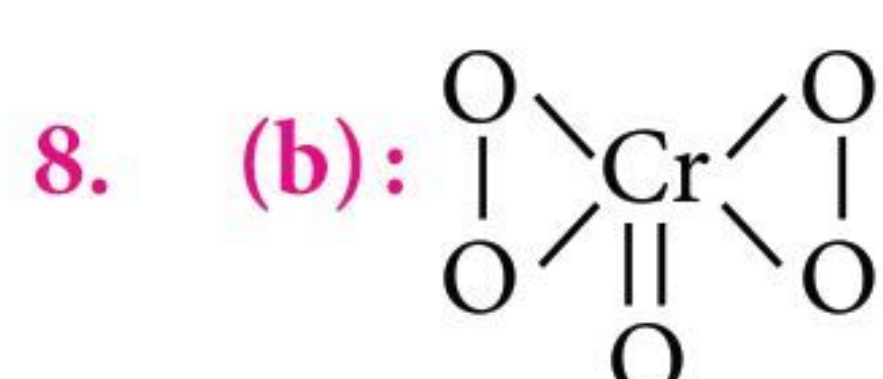
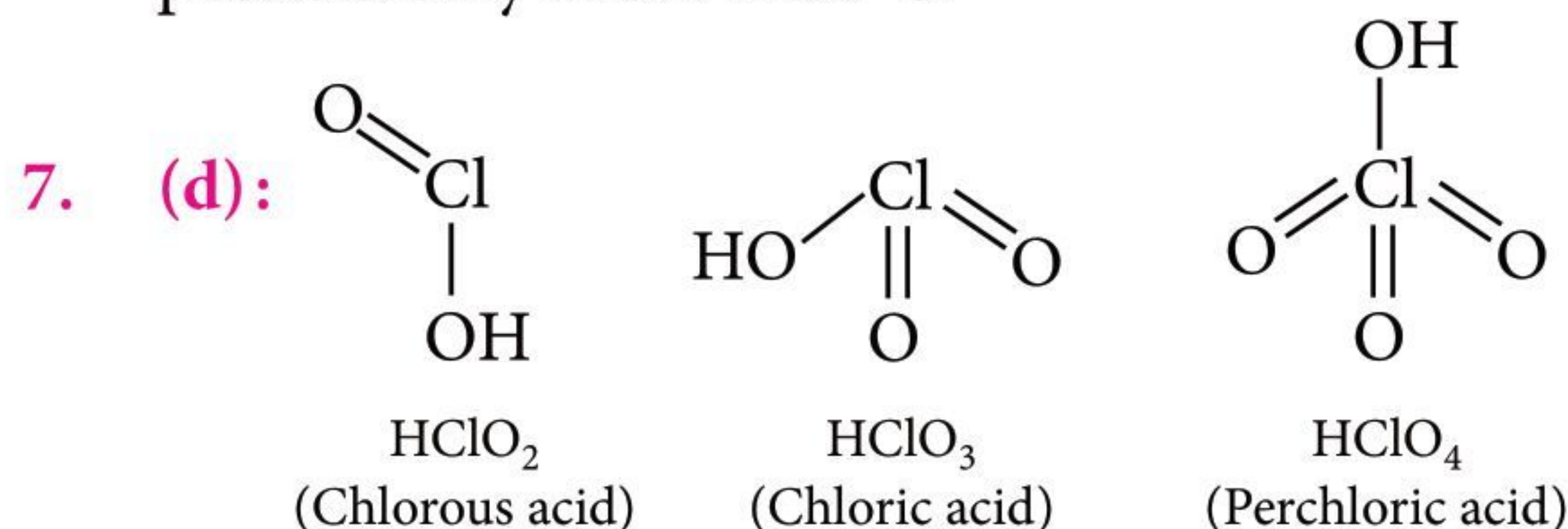
On substituting the values, $\frac{0.1}{0.8} = \left(\frac{50}{400} \right)^{n-1} = \left(\frac{1}{8} \right)^{n-1}$

Equating powers on both sides, $n - 1 = 1 \Rightarrow n = 2$

5. (c) : Zeta potential is potential difference between fixed charged layer and the diffused layer having opposite charges.

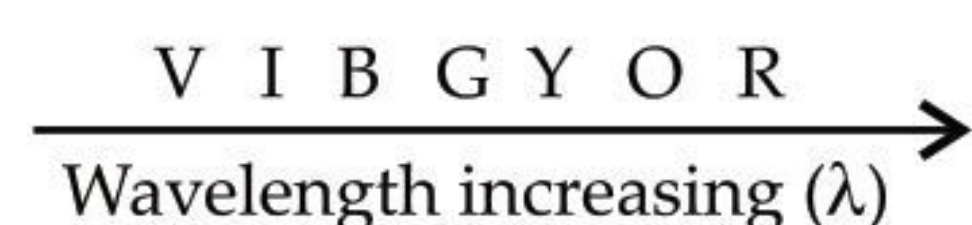


For this reaction, ΔG should be -ve which is possible only above 1400°C .

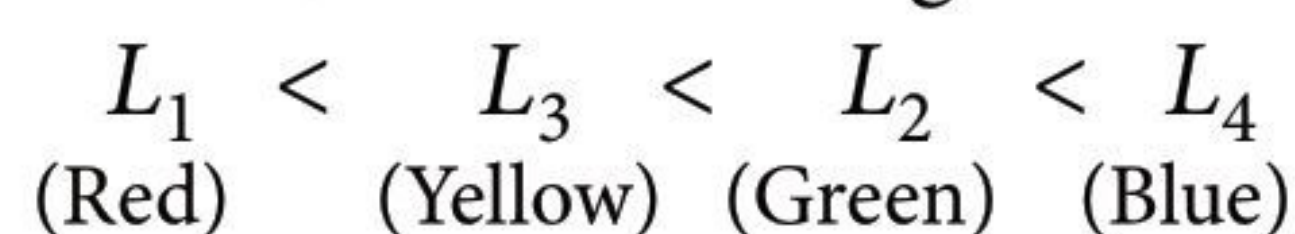


9. (c) : According to the spectrochemical series, more the absorption frequency, stronger is the ligand.

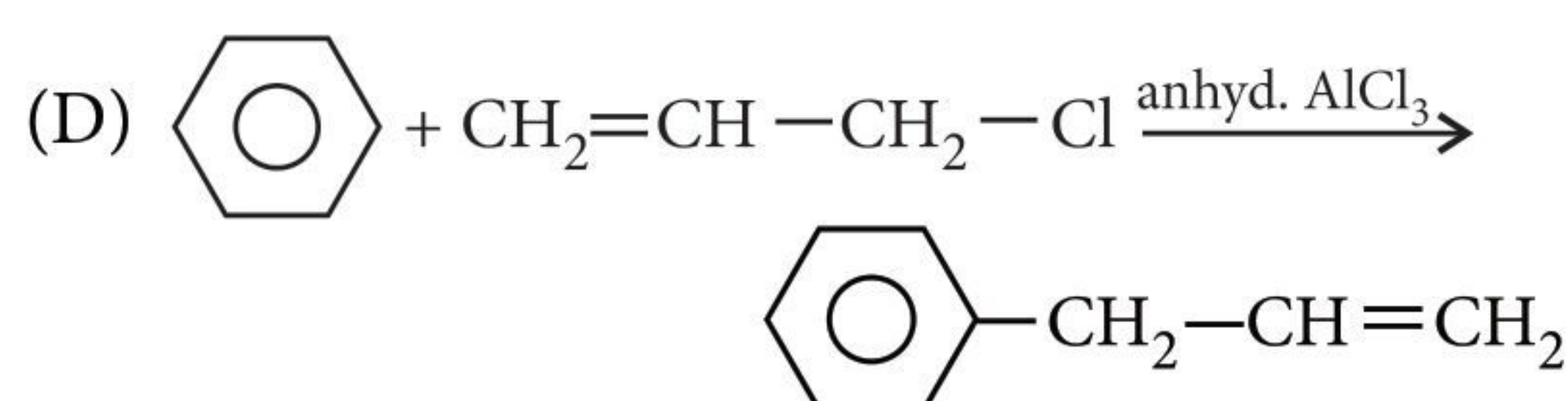
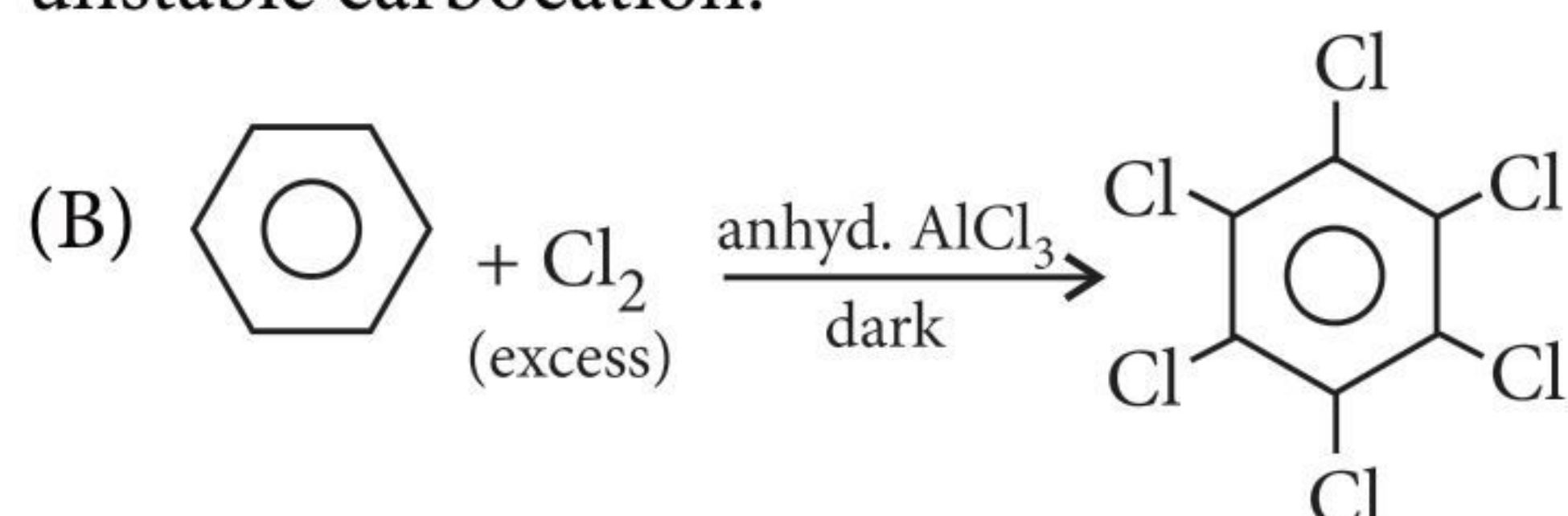
$$\Delta \text{ or CFSE} \propto \text{Strength of ligands} \propto \frac{1}{\lambda}$$



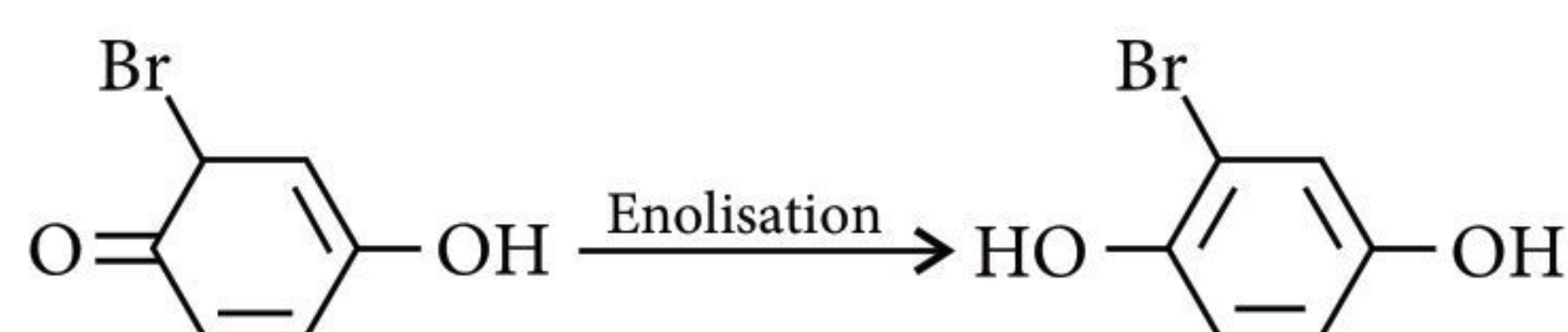
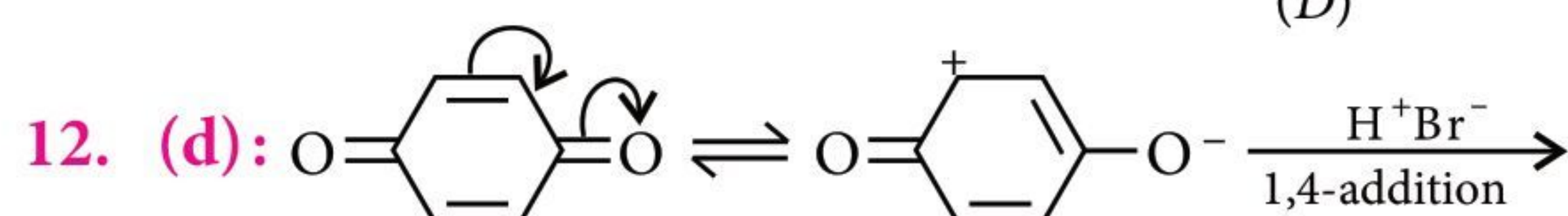
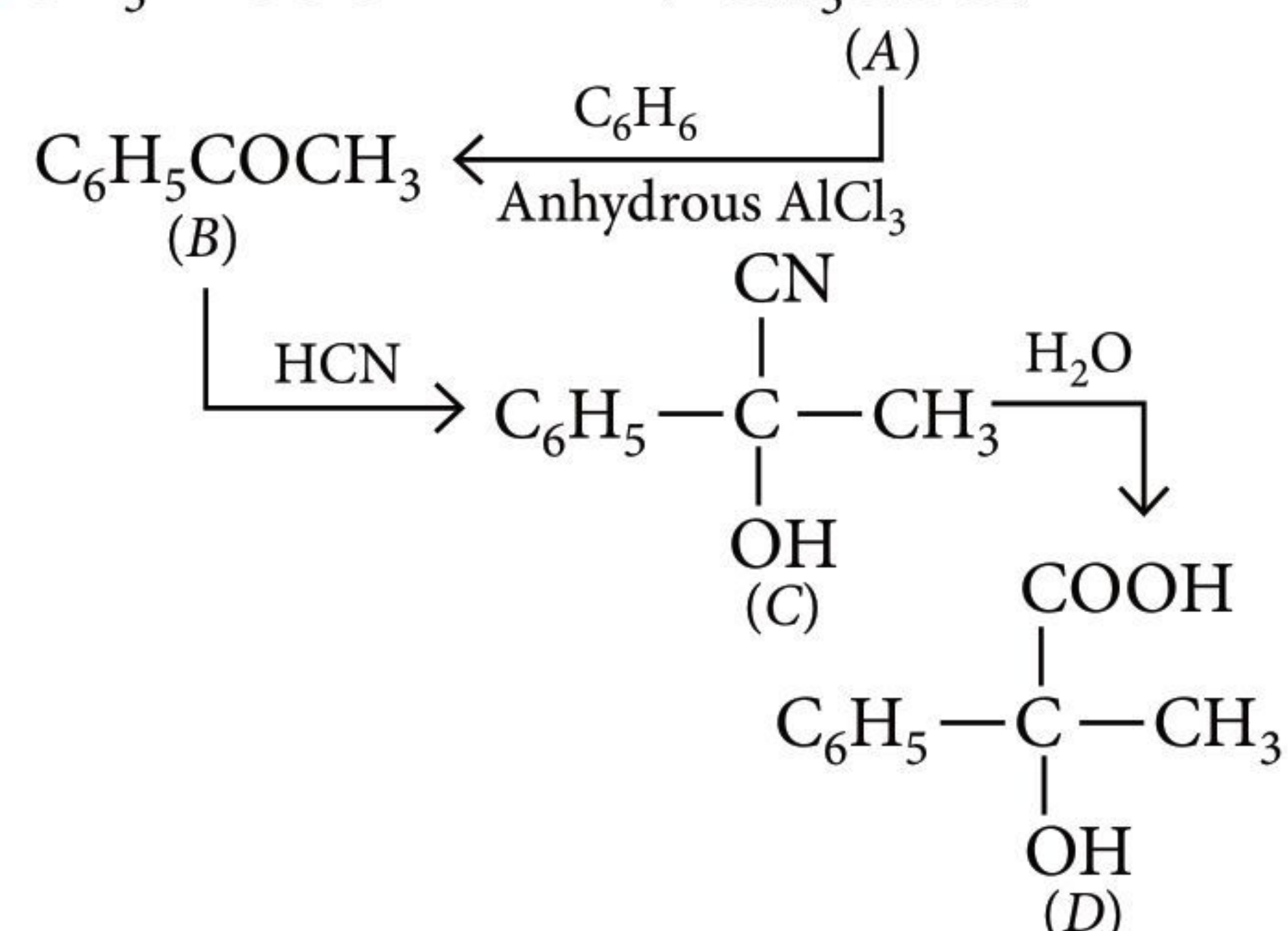
Hence, the increasing order of ligand strength is,



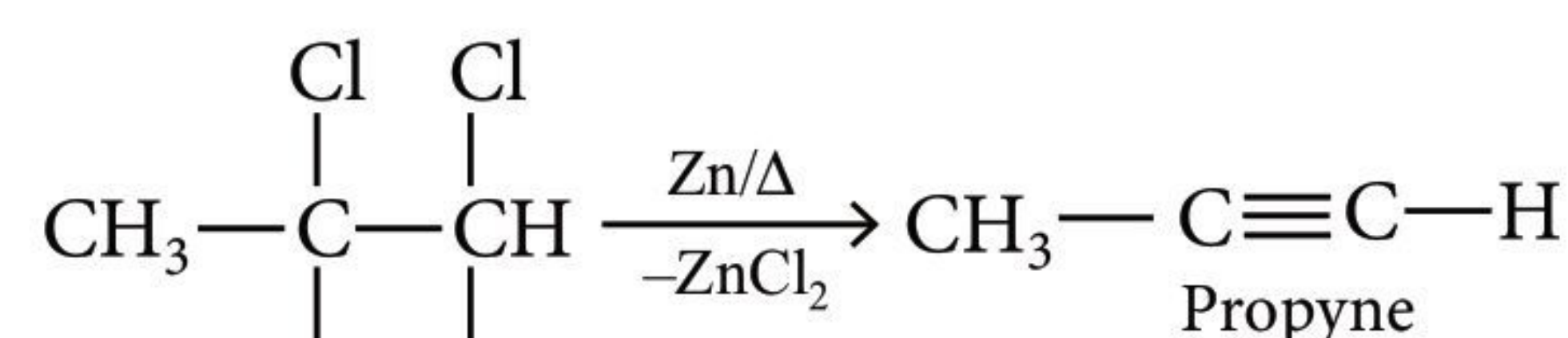
10. (b) : Aryl halide (A) and vinyl halide (C) do not give Friedel-Crafts reaction due to formation of unstable carbocation.



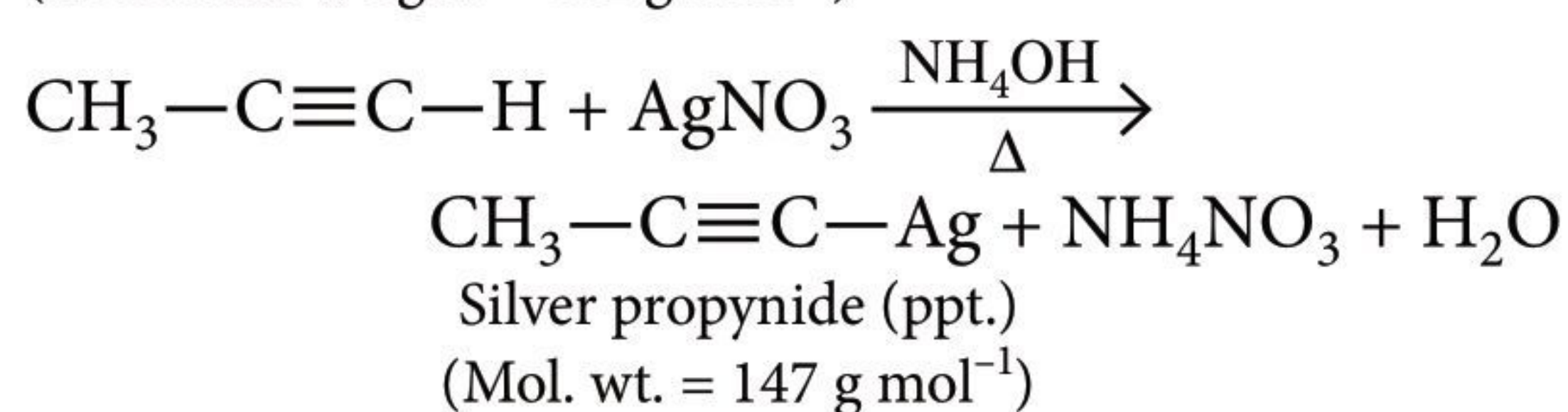
Thus, (B) and (D) are possible reactions.



13. (29.4) : The halogenation of vicinal tetrahaloalkane gives alkynes. It is done by heating the compound with Zn dust.



1, 1, 2, 2-Tetrachloropropane
 (Molecular weight = 182 g mol^{-1})



182 g of 1,1,2,2-tetrachloropropane gives 147 g of ppt.

\therefore 36.4 g of 1,1,2,2-tetrachloropropane gives

$$= \frac{147 \times 36.4}{182} = 29.4 \text{ g of precipitate}$$

14. (5) : Buna-S, PVC, natural rubber and Buna-N are formed by addition polymerisation.

15. (48931.6) : Osmotic pressure (π) = $\frac{w}{MV} RT$

$$M = \frac{w}{\pi V} RT = \frac{10}{5 \times 10^{-3} \times 1} \times 0.0821 \times 298$$

$$= 48931.6 \text{ g/mol}$$

CONCEPT MAP

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Carboxylic Acids

General Methods of Preparation

Chemical Properties

Introduction

Compounds containing >C=O group are called carbonyl compounds. These are aldehydes, $\left(\text{R}>\text{C=O}\right)$, ketones $\left(\text{R}>\text{C=O}\right)$, carboxylic acids $\left(\text{HO}>\text{C=O}\right)$, acid chlorides $\left(\text{Cl}>\text{C=O}\right)$, esters $\left(\text{RO}>\text{C=O}\right)$, amides $\left(\text{H}_2\text{N}>\text{C=O}\right)$ and acid anhydride $\left(\text{O}>\text{C-O-C}>\text{O}\right)$.

Physical Properties

- Physical state :** Formaldehyde is a pungent smelling gas. Aldehydes and ketones upto eleven carbon atoms are colourless liquids and higher members are solids.
- Smell :** The odour of lower aldehydes is unpleasant but the odour of higher aldehydes is pleasant.
- Boiling point :** The boiling point of aldehydes and ketones rise steadily with increase in molecular mass. Among carbonyl compounds, ketones have slightly higher b.pt. than isomeric aldehydes. This is due to the presence of two electron releasing groups around the carbonyl carbon which makes them more polar.
- Solubility :** Lower members are soluble in water, whereas higher members are insoluble in water. Aldehydes and ketones are however soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

Distinction between Aldehydes and Ketones

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Grey precipitate of silver or silver mirror	No grey ppt. or silver mirror

Aldehydes and Ketones

General Methods of Preparation

- Oxidation of alcohols :**

$$\text{RCH}_2\text{OH} + [\text{O}] \xrightarrow[\text{PDC}]{\text{PCC}} \text{RCHO} + \text{H}_2\text{O}$$

$$\text{R}_2\text{CHOH} + [\text{O}] \xrightarrow[\text{PDC}]{\text{PCC}} \text{R}-\text{C}(=\text{O})-\text{R} + \text{H}_2\text{O}$$
- Rosenmund reduction :**

$$\text{RCOCl} + \text{H}_2 \xrightarrow[\text{boiling xylene}]{\text{Pd-BaSO}_4, \text{S}} \text{RCHO} + \text{HCl}$$
- Reduction of nitriles followed by hydrolysis :**

$$\text{RC}\equiv\text{N} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) AlH}(\text{i-Bu})_2} \text{RCHO}$$

$$\text{RC}\equiv\text{N} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) R'MgX/dry ether}} \text{RCOR'}$$

$$\text{RC}\equiv\text{N} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) SnCl}_2 + \text{HCl}} \text{RCHO} + \text{NH}_4\text{Cl} \quad (\text{Stephen reduction})$$
- Gatterman-Koch reaction :**

$$\text{C}_6\text{H}_6 \xrightarrow[\text{Anhyd. AlCl}_3, \text{CuCl}]{\text{CO, HCl}} \text{C}_6\text{H}_5\text{CHO}$$
- Friedel-Crafts acylation :**

$$\text{C}_6\text{H}_6 \xrightarrow[\text{Anhyd. AlCl}_3]{\text{RCOCl}} \text{C}_6\text{H}_5\text{COR}$$
- Etard reaction :**

$$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CrO}_2\text{Cl}_2/\text{CS}_2} \text{C}_6\text{H}_5\text{CHO}$$
- Side chain chlorination followed by hydrolysis:**

$$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow[\text{(ii) H}_2\text{O, 373 K}]{\text{(i) Cl}_2/\text{hv}} \text{C}_6\text{H}_5\text{CHO}$$

Chemical Properties

- Nucleophilic addition reactions :**

$$\text{>C=O} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) RMgX}} \text{>C}(\text{R})\text{OH}$$

$$\text{>C=O} \xrightarrow[\text{dry HCl}]{\text{ROH}} \text{>C}(\text{OR})\text{OH} \xrightarrow[\text{dry HCl}]{\text{ROH}} \text{>C}(\text{OR})_2$$

Hemiacetal Acetal
- Nucleophilic addition-elimination reactions :**

$$\text{>C=O} \xrightarrow[\text{(ii) } \Delta]{\text{(i) NH}_3} \text{>C=NH} \quad \text{Imine}$$

$$\text{>C=O} \xrightarrow[\text{(ii) } \Delta]{\text{(i) NH}_2-\text{Z}} \text{>C=N-Z}$$

[where, Z = Alkyl, Aryl, -OH, -NH₂, -NHC₆H₅, -NH-C₆H₄-NO₂, -NHCONH₂]
- Haloform reaction :**

$$2\text{NaOH} + \text{I}_2 \longrightarrow \text{NaI} + \text{NaOI} + \text{H}_2\text{O}$$

$$\text{RCOCH}_3 + 3\text{NaOI} \longrightarrow \text{RCOONa} + \text{CHI}_3 \downarrow + 2\text{NaOH}$$

Iodoform (yellow ppt.)

(Given by compounds having CH₃CO-group or CH₃CH(OH)-group).
- Aldol condensation reaction :**

$$2\text{R}-\text{CH}_2-\text{C}(=\text{O})-\text{H} \xrightarrow[\text{dil. NaOH}]{\text{OH}^-} \text{R}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{R})-\text{C}(=\text{O})-\text{H}$$

Aldol

$$\text{R}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{R})-\text{C}(=\text{O})-\text{H} \xrightarrow[\Delta]{-\text{H}_2\text{O}} \text{R}-\text{CH}_2-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{H}$$

α,β -Unsaturated aldehyde

(Aldehydes and ketones having at least one α -hydrogen give such reaction.)
- Cannizzaro reaction :**

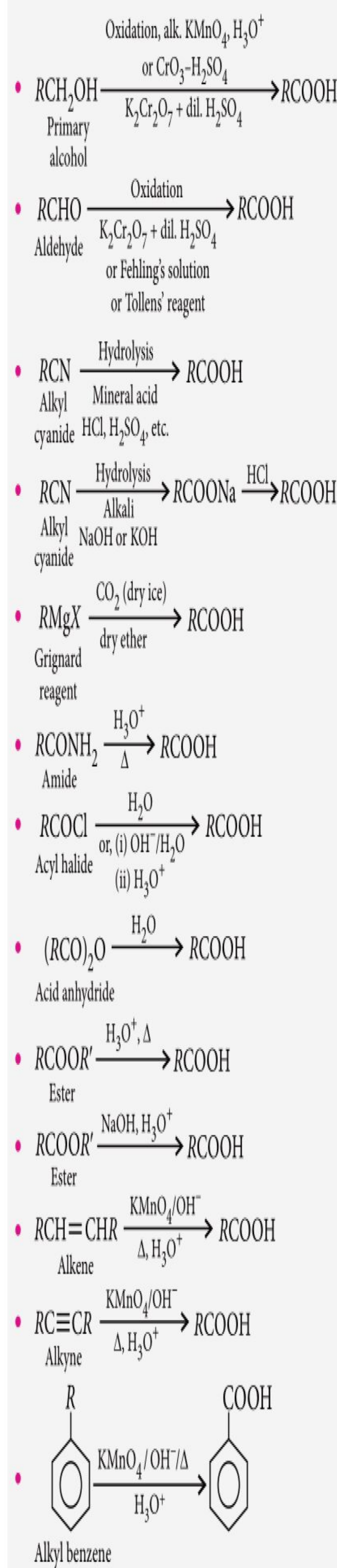
$$\text{HCHO} + \text{HCHO} \xrightarrow[\text{KOH}]{\text{conc.}} \text{CH}_3\text{OH} + \text{HCOO}^- \text{K}^+$$

Formaldehyde Methanol Potassium formate

(Aldehydes which do not have an α -hydrogen atom give such reaction.)
- Crossed Cannizzaro reaction :**

$$\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{H} + \text{H}-\text{C}(=\text{O})-\text{H} \xrightarrow[\Delta]{\text{OH}^-} \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{HCOO}^- \text{Na}^+$$

Benzyl alcohol Sod. formate
- Intramolecular Cannizzaro reaction :** It is given by dialdehydes having no α -hydrogen atoms.

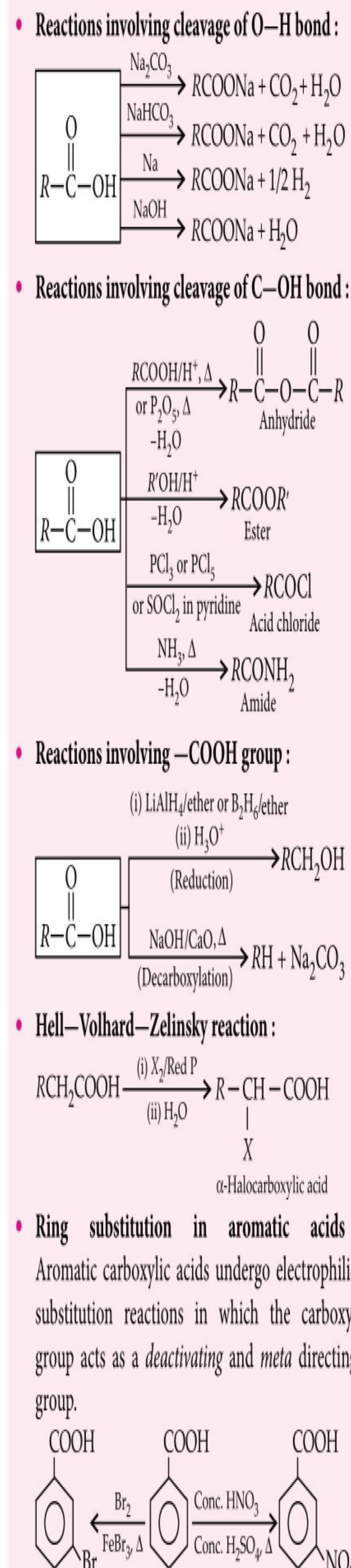


Physical Properties

- Aliphatic carboxylic acids upto nine carbon atoms are colourless, odourless liquids.
- The higher acids are wax like solids.
- Carboxylic acids have higher boiling points than the aldehydes, ketones and even alcohols of comparable molecular masses. The higher boiling point is due to extensive bonding of carboxylic acid molecules through intermolecular hydrogen bonding. Most of the carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.
- Aliphatic carboxylic acids upto four carbon atoms are miscible in water due to the formation of intermolecular hydrogen bonds with water.
- Solubility decreases with increasing number of C atoms.
- Higher carboxylic acids are insoluble in water due to the higher hydrophobic interaction of alkyl group.
- Aromatic acids are insoluble in water. Benzoic acid is soluble in hot water but insoluble in cold water.
- Carboxylic acids are soluble in less-polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Distinction between Phenol and Carboxylic Acid

Test	Phenol	Carboxylic acid
NaHCO ₃ test	No reaction	Brisk effervescence of CO ₂ gas.
FeCl ₃ test	Violet colour	Buff coloured ppt.



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Unit
8

Biomolecules | Polymers | Chemistry in Everyday Life

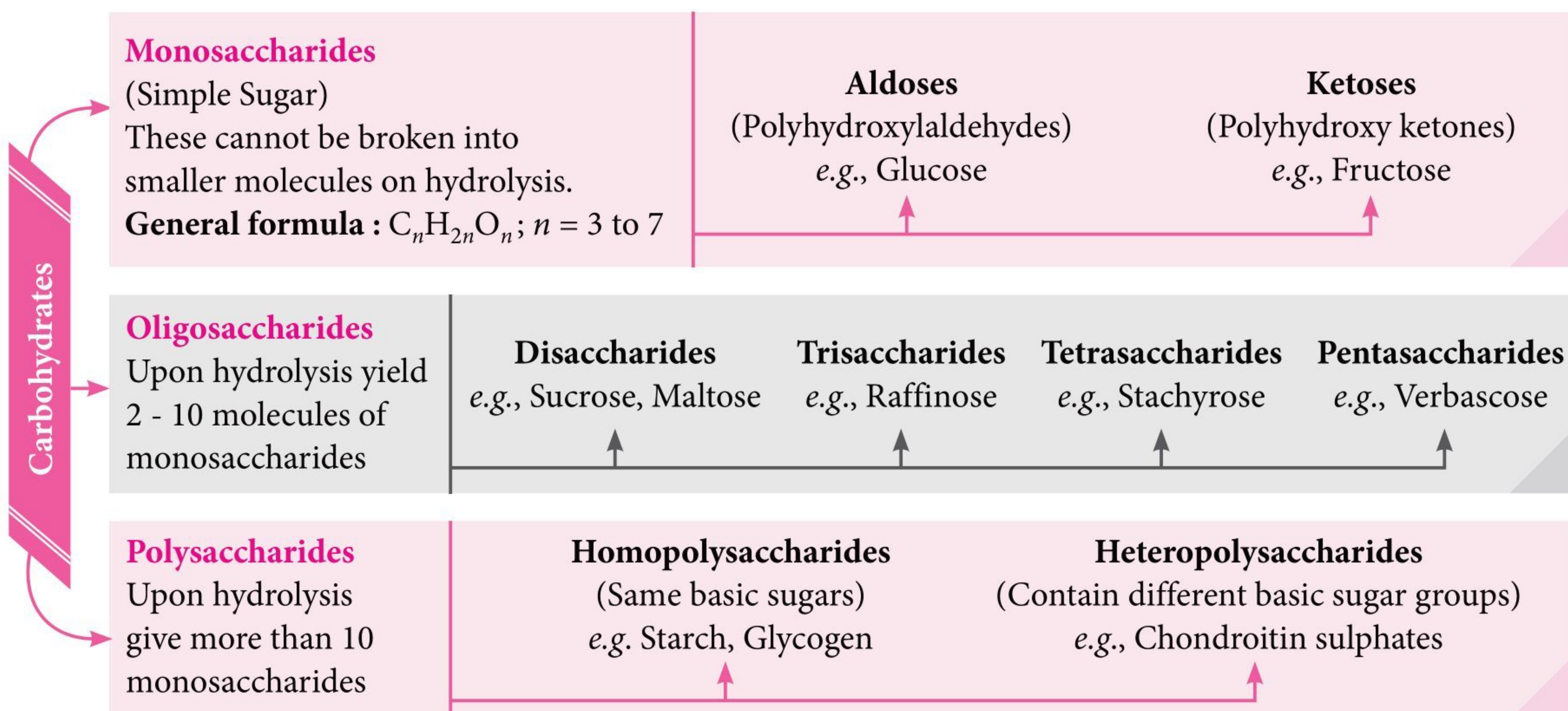
Biomolecules

- Biomolecules are complex, organic molecules (compounds) which combine in a specific manner to produce life, *e.g.*, carbohydrates, proteins, nucleic acids, lipids, etc. Some simple molecules like vitamins and mineral salts also play an important role in the functions performed by organisms.

CARBOHYDRATES

- Carbohydrates are polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis and contain at least one chiral C-atom in their molecules. They have the general formula $C_x(H_2O)_y$ *e.g.*, glucose, fructose, sucrose, etc.

Classification

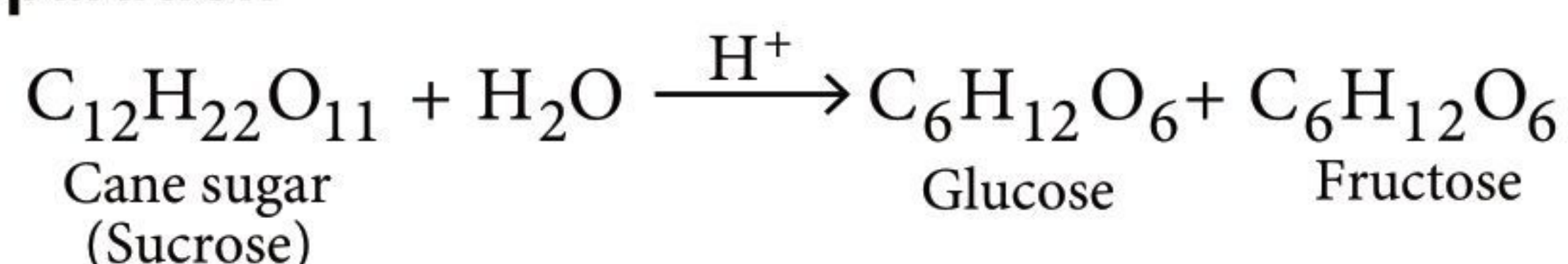


MONOSACCHARIDES

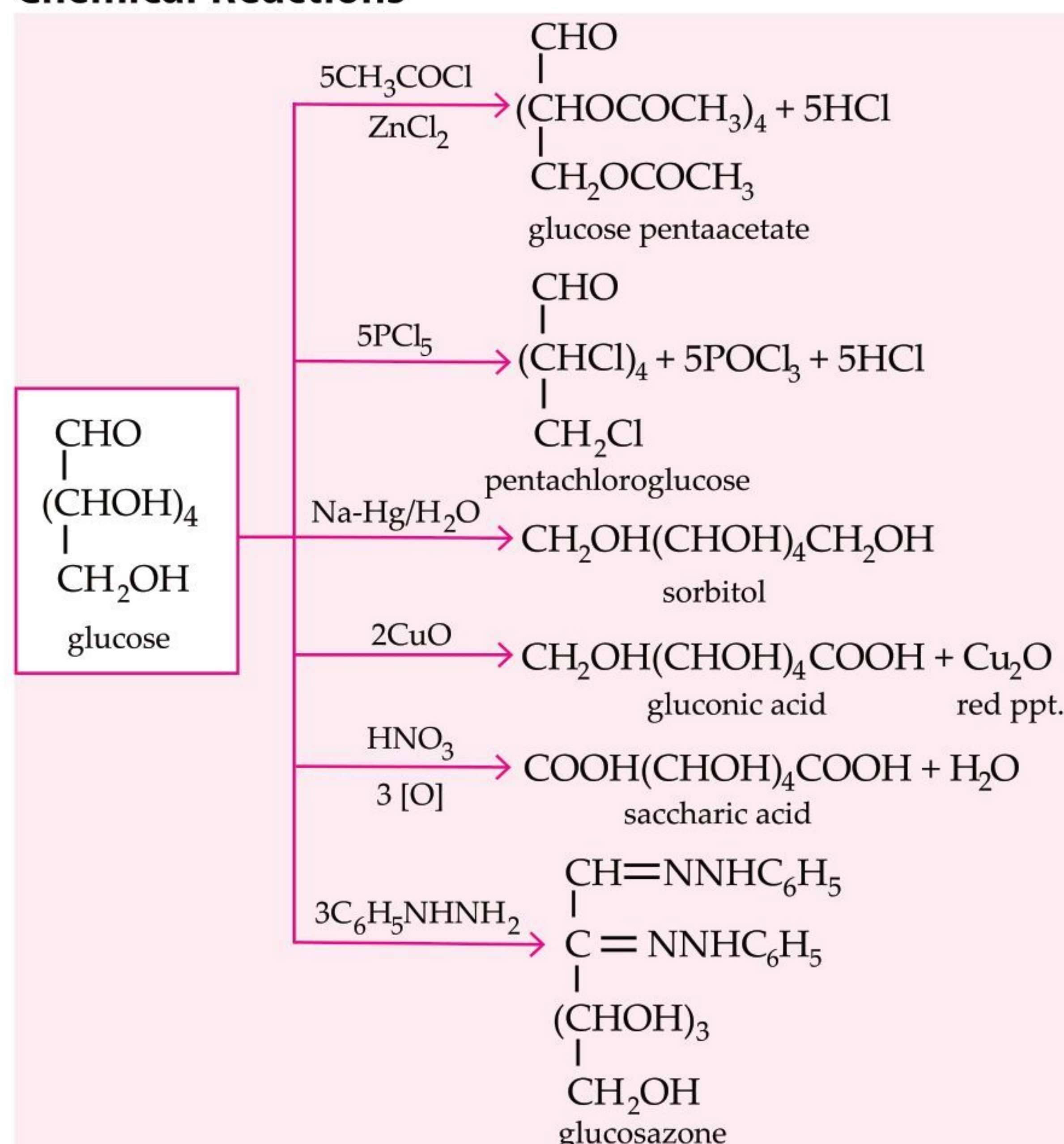
- Glucose ($C_6H_{12}O_6$)** : It occurs in ripe grapes, honey and in most of the sweet fruits. Glucose is known as

dextrose because it occurs in nature as the optically active dextrorotatory isomer.

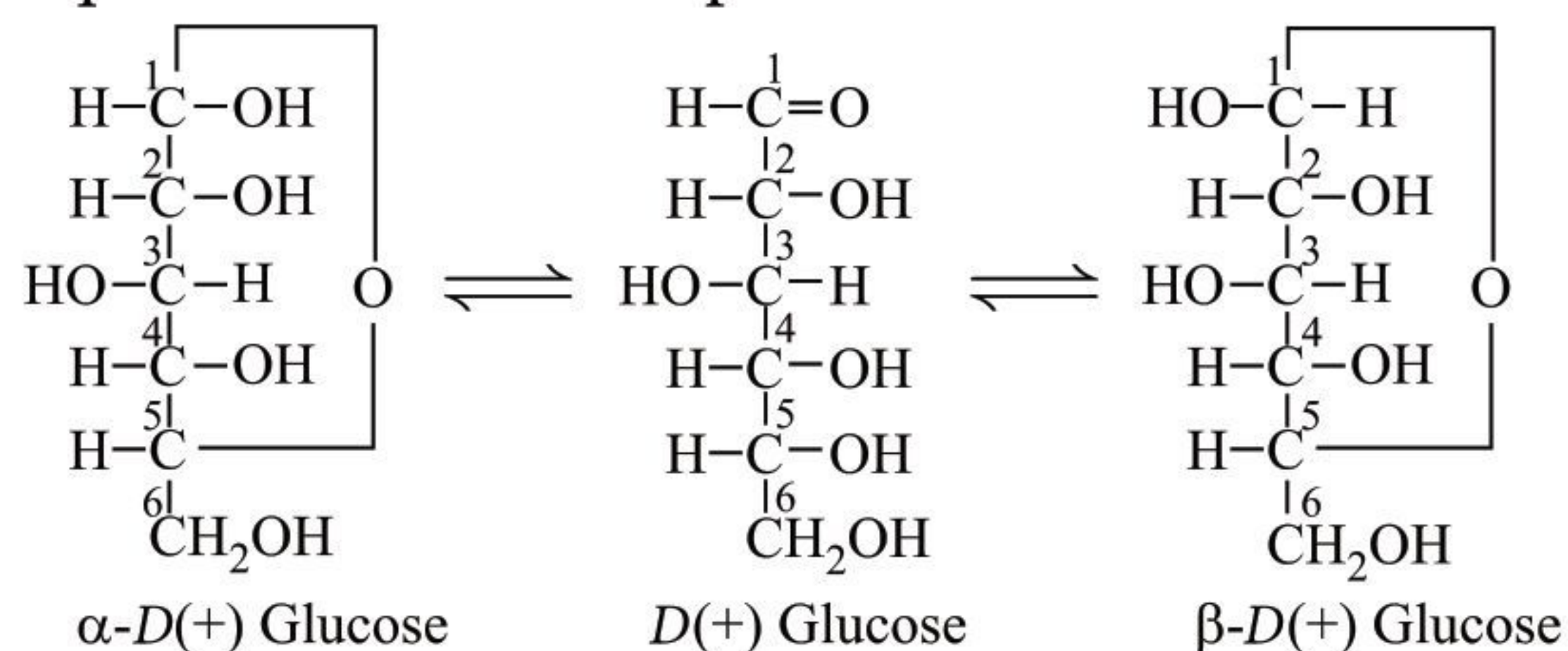
Preparation



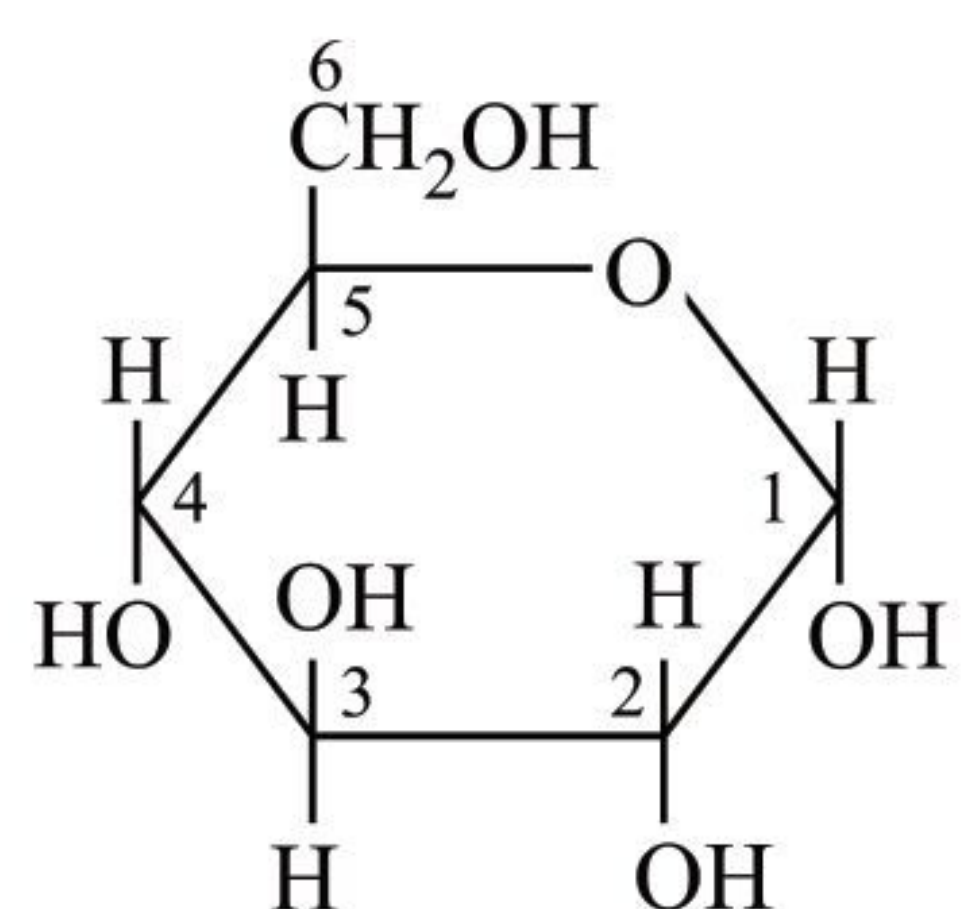
Chemical Reactions



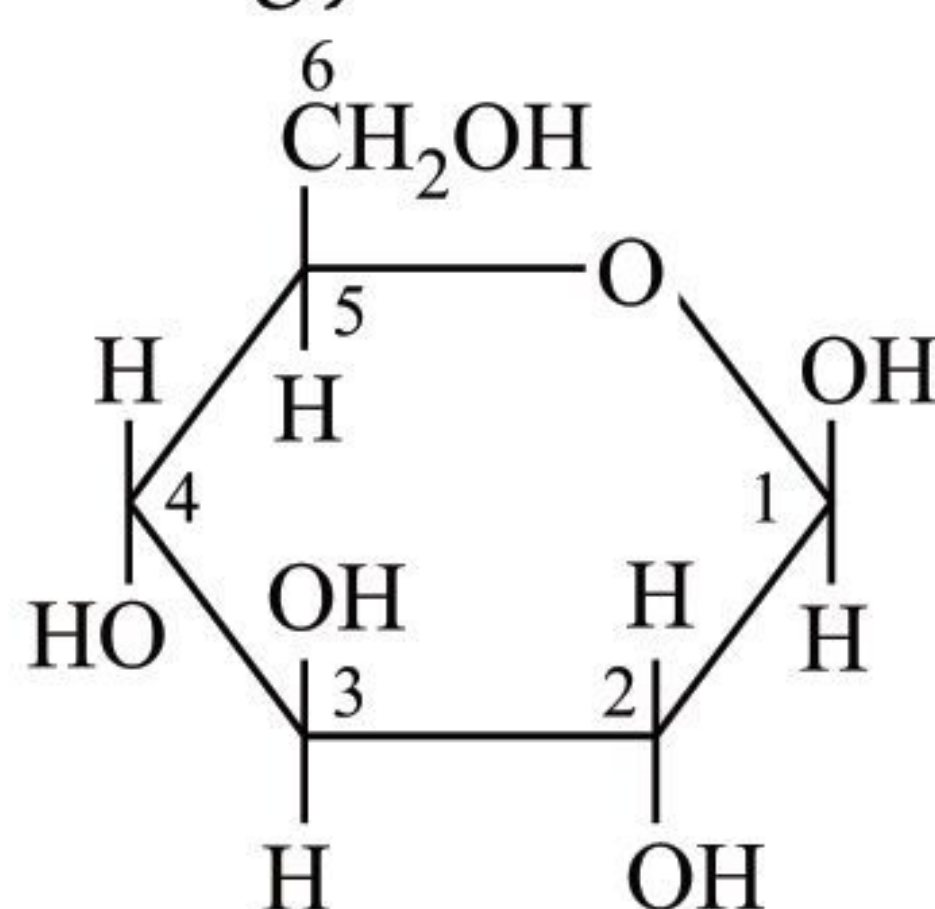
- The straight chain form of glucose exists in equilibrium with the open chain form.



- The five membered and six membered ring containing an oxygen atom is called *furanose* & *pyranose form* respectively.
- Anomers** refer to a pair of stereoisomers which differ in configuration only around C-1 and this C-1 carbon is called *anomeric carbon* or *glycosidic carbon*.

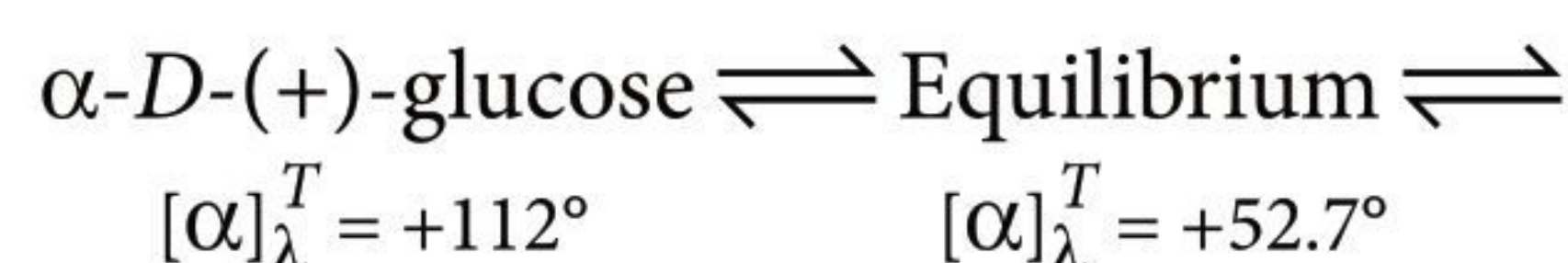


α-D(+) Glucose or
α-D(+) Glucopyranose

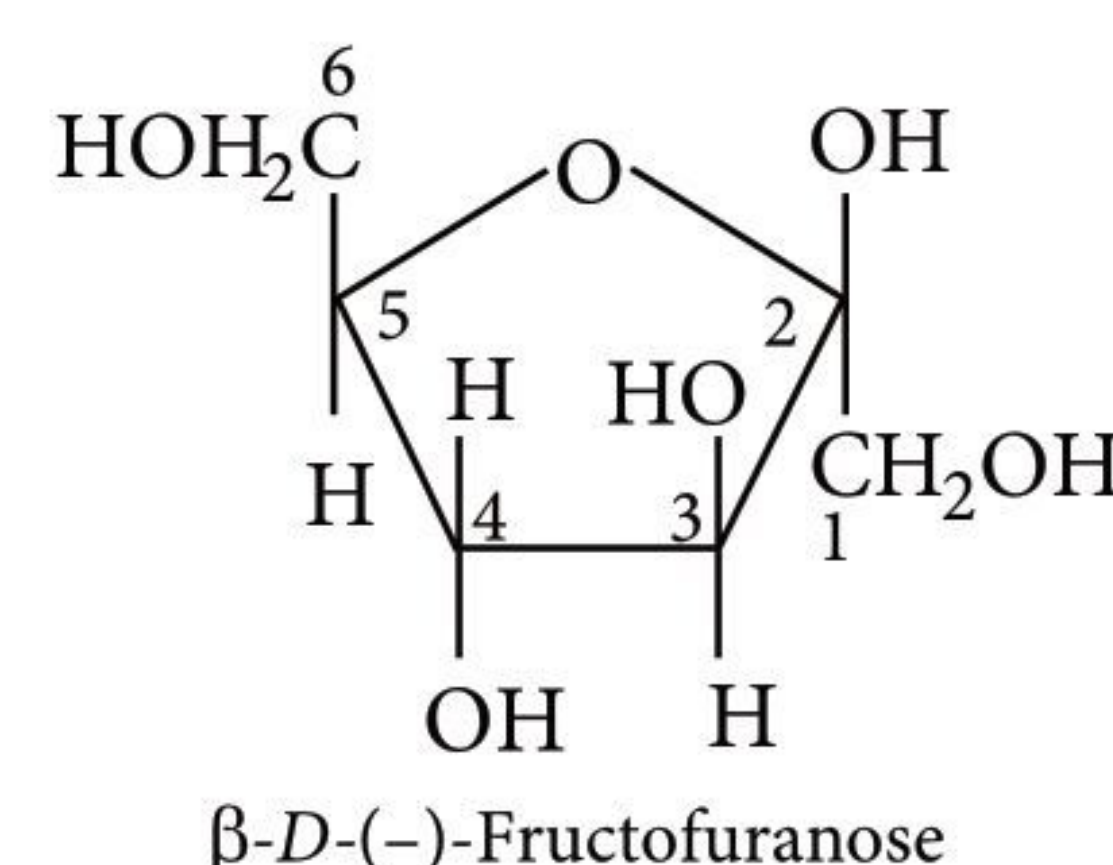
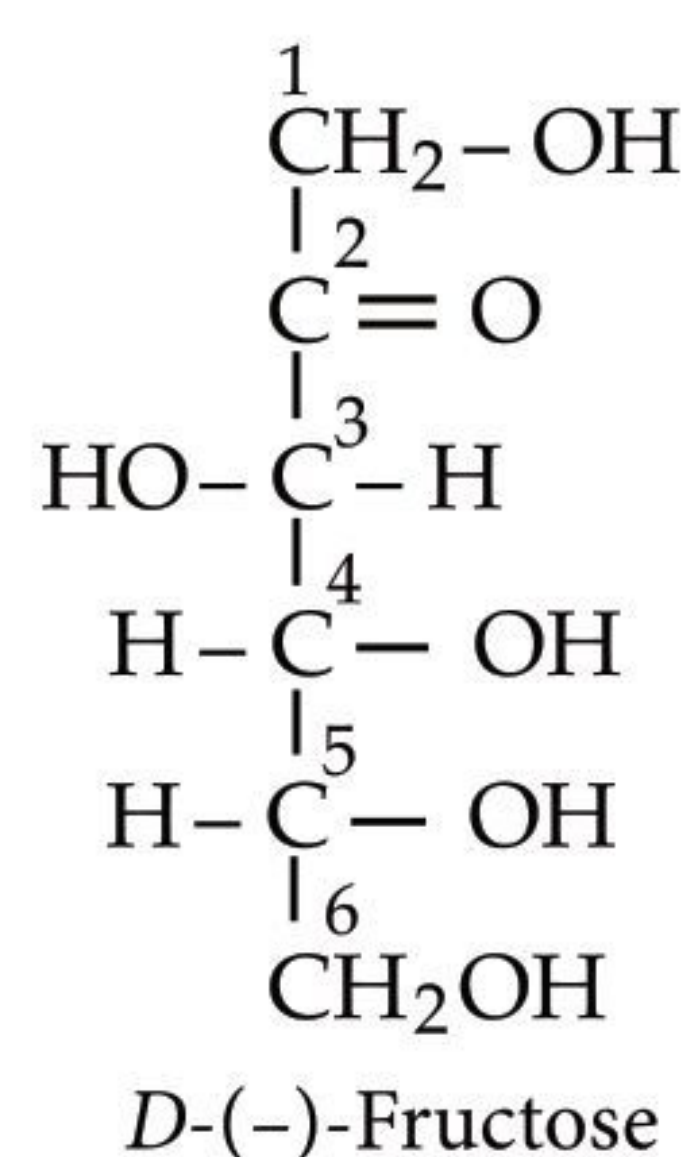


β-D(+) Glucose or
β-D(+) Glucopyranose

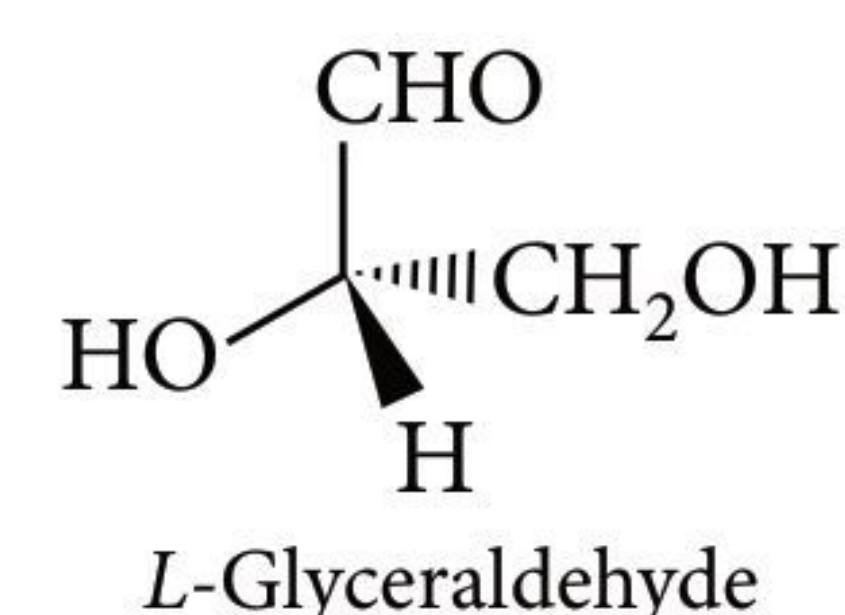
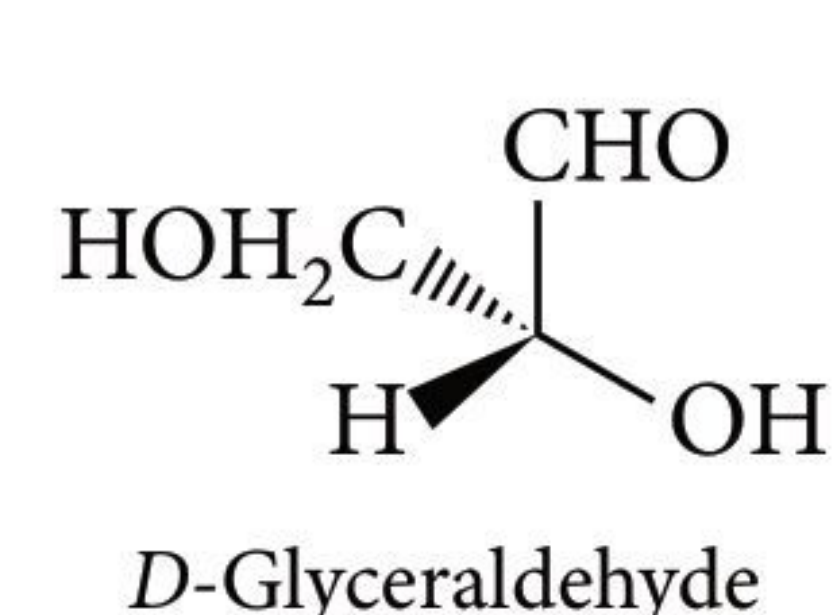
- Mutarotation** : The change in specific rotation of isomers of glucose in aqueous solution is called *mutarotation*.



- Fructose (C₆H₁₂O₆)** : It is present in abundance in fruits. Since naturally occurring fructose is laevorotatory, it is known as *laevulose*.



D and L Configuration



By convention, a monosaccharide is said to have *D*-configuration if the hydroxyl group attached to the asymmetric carbon atom adjacent to the —CH₂OH group is on the right hand side irrespective of the positions of the other hydroxyl groups. On the other hand, the molecule is assigned *L*-configuration if the —OH group attached to the carbon adjacent to the —CH₂OH group is on the left.

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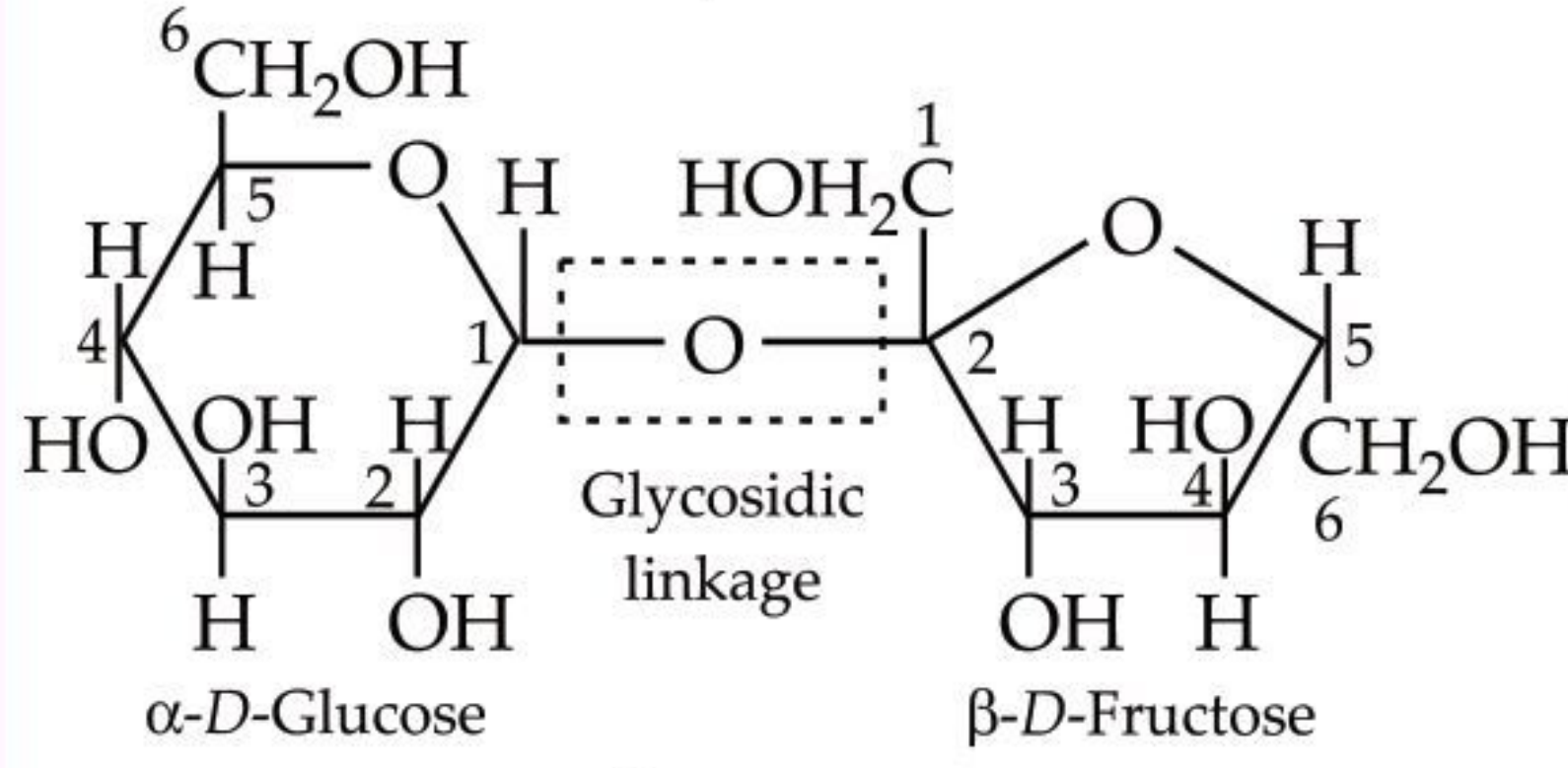
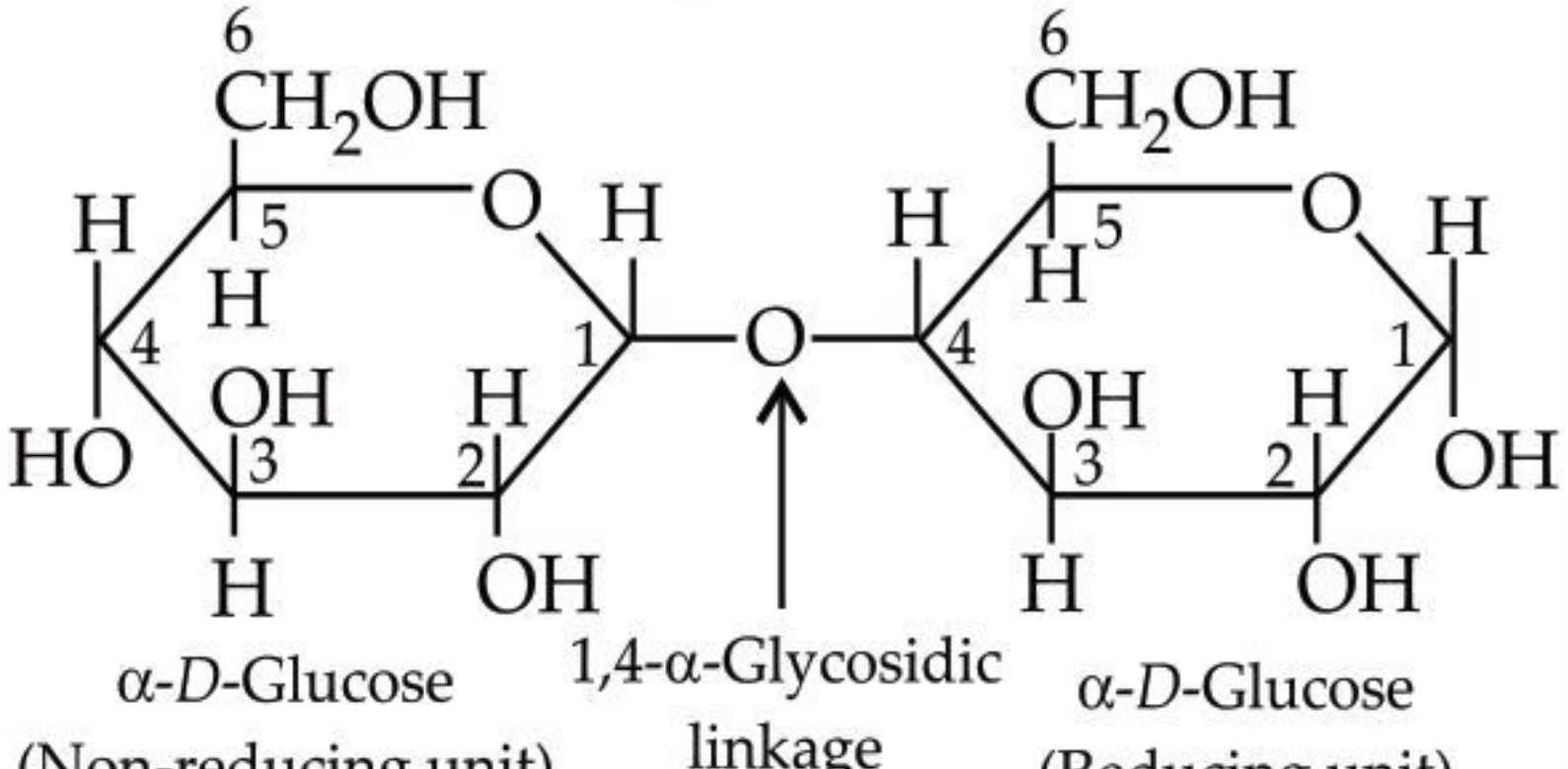
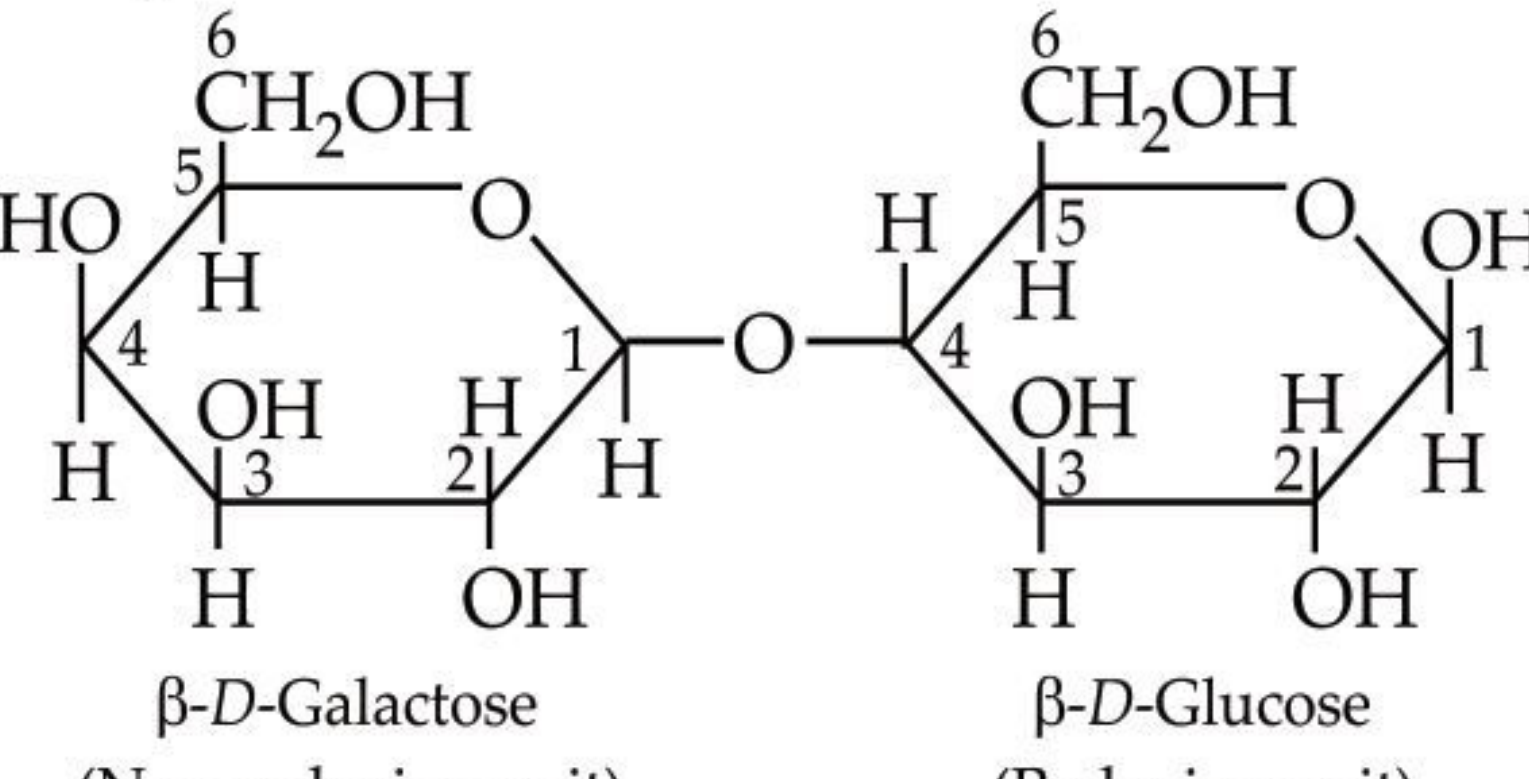
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DISACCHARIDES

Sucrose (C ₁₂ H ₂₂ O ₁₁)	Maltose (C ₁₂ H ₂₂ O ₁₁)	Lactose (C ₁₂ H ₂₂ O ₁₁)
<ul style="list-style-type: none"> • Cane sugar • Non-reducing sugar • Dextrorotatory  <p style="text-align: center;">Sucrose</p>	<ul style="list-style-type: none"> • Malt sugar • Reducing sugar • Dextrorotatory  <p style="text-align: center;">Maltose</p>	<ul style="list-style-type: none"> • Milk sugar • Reducing sugar • Epimeric in nature  <p style="text-align: center;">Lactose</p>

POLYSACCHARIDES

Starch

- It is a polymer of α -glucose and consists of two components - **amylose** and **amylopectin**.

	Amylose	Amylopectin
1.	It is water soluble.	It is insoluble in water.
2.	It is 15-20% of starch.	It is 80-85% of starch.
3.	It is long straight chain polymer.	It is long branched chain polymer.
4.	It has 200-1000 α -D-glucose units held by C ₁ -C ₄ glycosidic linkage.	It has 2000-3000 α -D-glucose units joined by C ₁ -C ₆ glycosidic linkage. It consists of short chains containing 20-25 glucose units, connected with each other by 1,4- α -glycosidic linkage.
5.	It gives blue colour with iodine solution.	It does not give blue colour with iodine solution.

Cellulose

- It is the structural material of cell walls of all the plants. It is also the chief component of cotton, wood and jute. Cellulose on hydrolysis with dil. H₂SO₄ and under pressure gives only β -D-(+)-glucose. β -D-(+)-glucose units in cellulose are joined to each other by glycosidic linkage between C-1 of one glucose unit and C-4 of the next glucose unit.

Glycogen

The carbohydrates are stored in animal body as glycogen. It is also known as *animal starch* because

its structure is similar to amylopectin and is rather more highly branched. When the body needs glucose, enzymes break the glycogen down to glucose.

PROTEINS

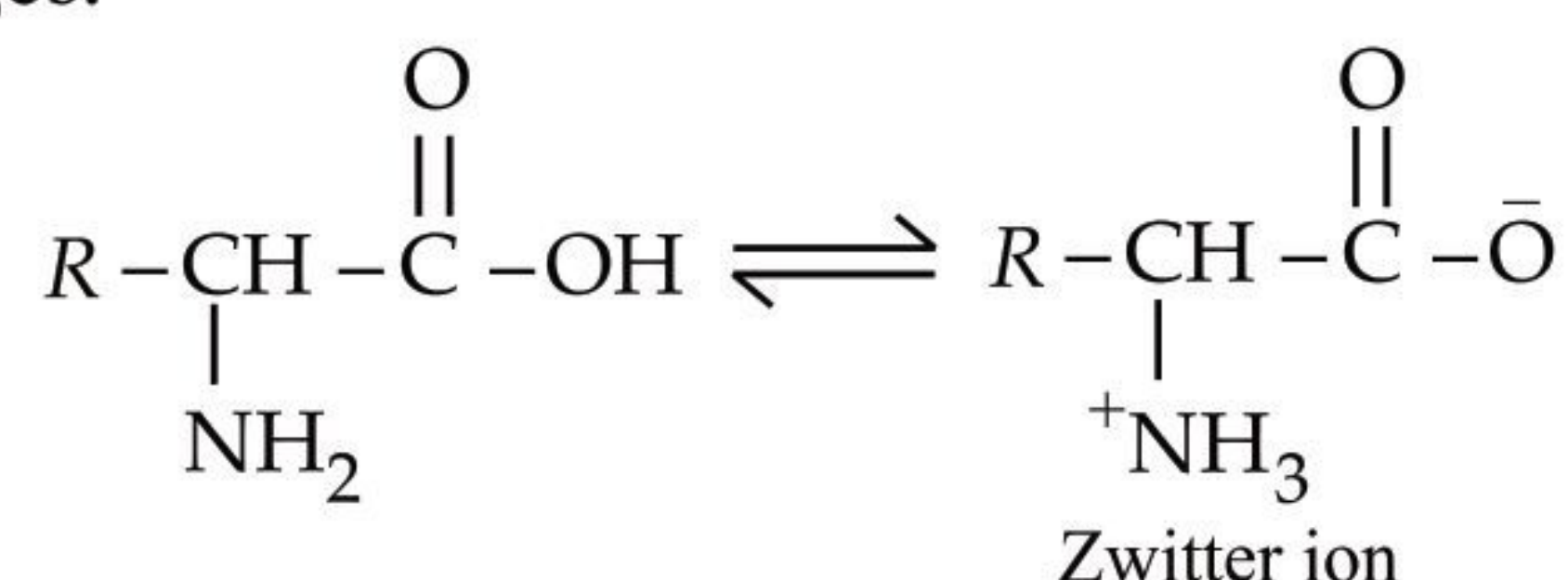
- Proteins are high molecular mass complex biomolecules of α -amino acids present in all living cells. They are vital chemical substances essential for growth and maintenance of life.
- Amino acids are organic compounds containing both an amino group and a carboxylic group.



α -Amino acids are those, in which the amino group is located on the carbon atom adjacent to the carboxyl group (α -carbon atom).

Physical Properties of α -Amino acids

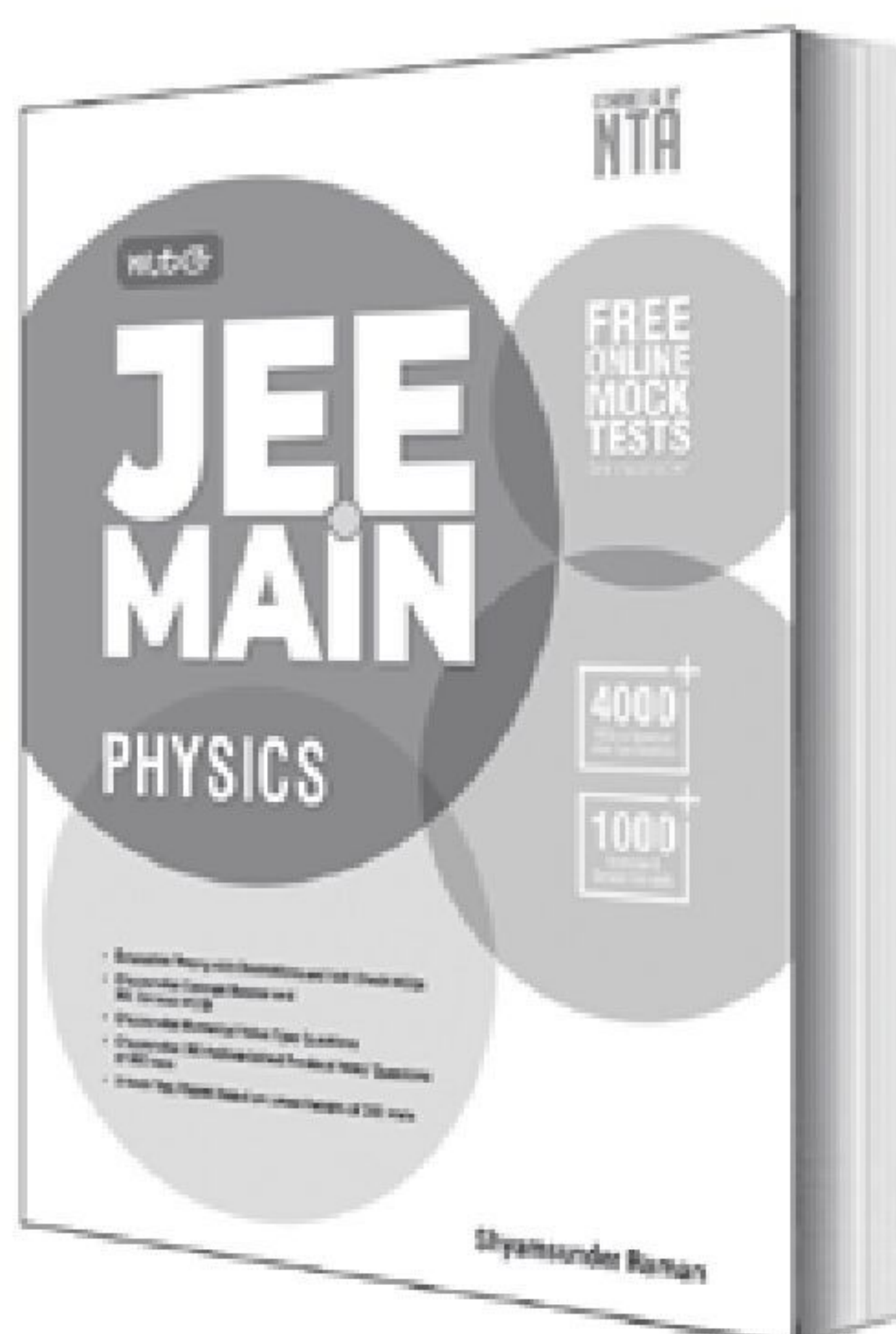
- Amino acids are usually colourless, crystalline water soluble and high melting solids.
- They behave like salts due to presence of basic amino group ($-NH_2$) and acidic carboxylic group ($-COOH$) in the same molecule.
- In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as **zwitter ion**. This is neutral but contains both positive and negative charges.



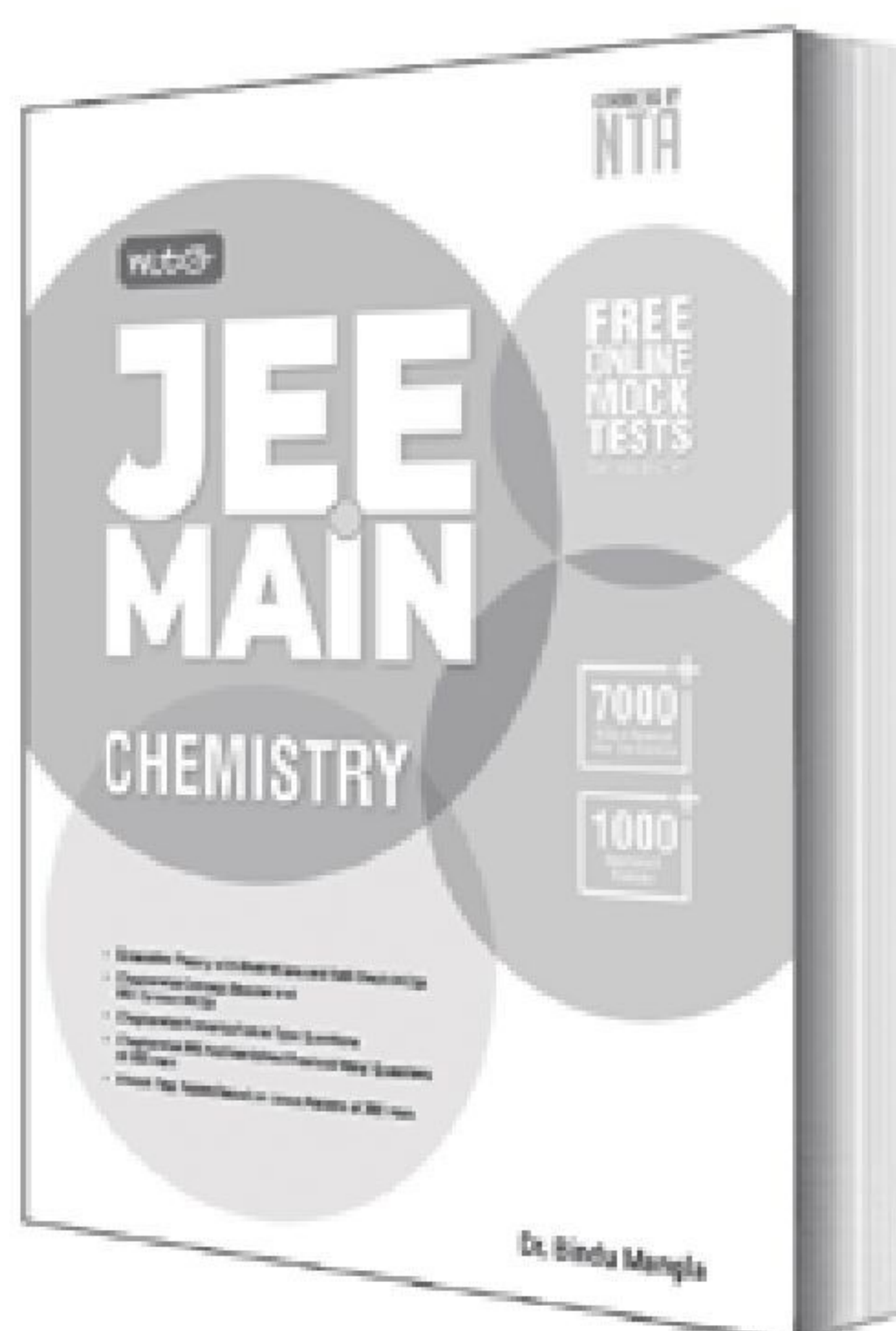
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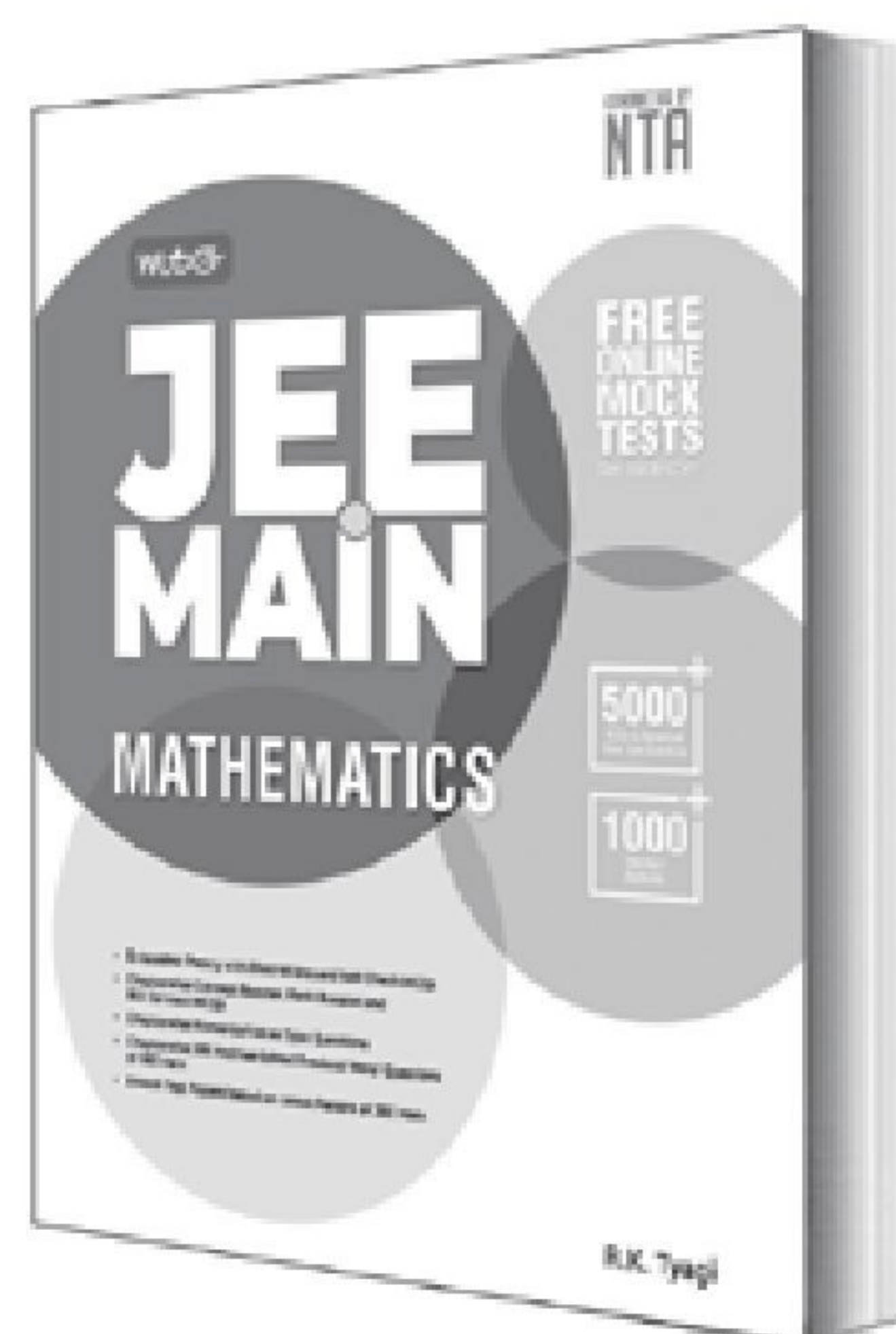
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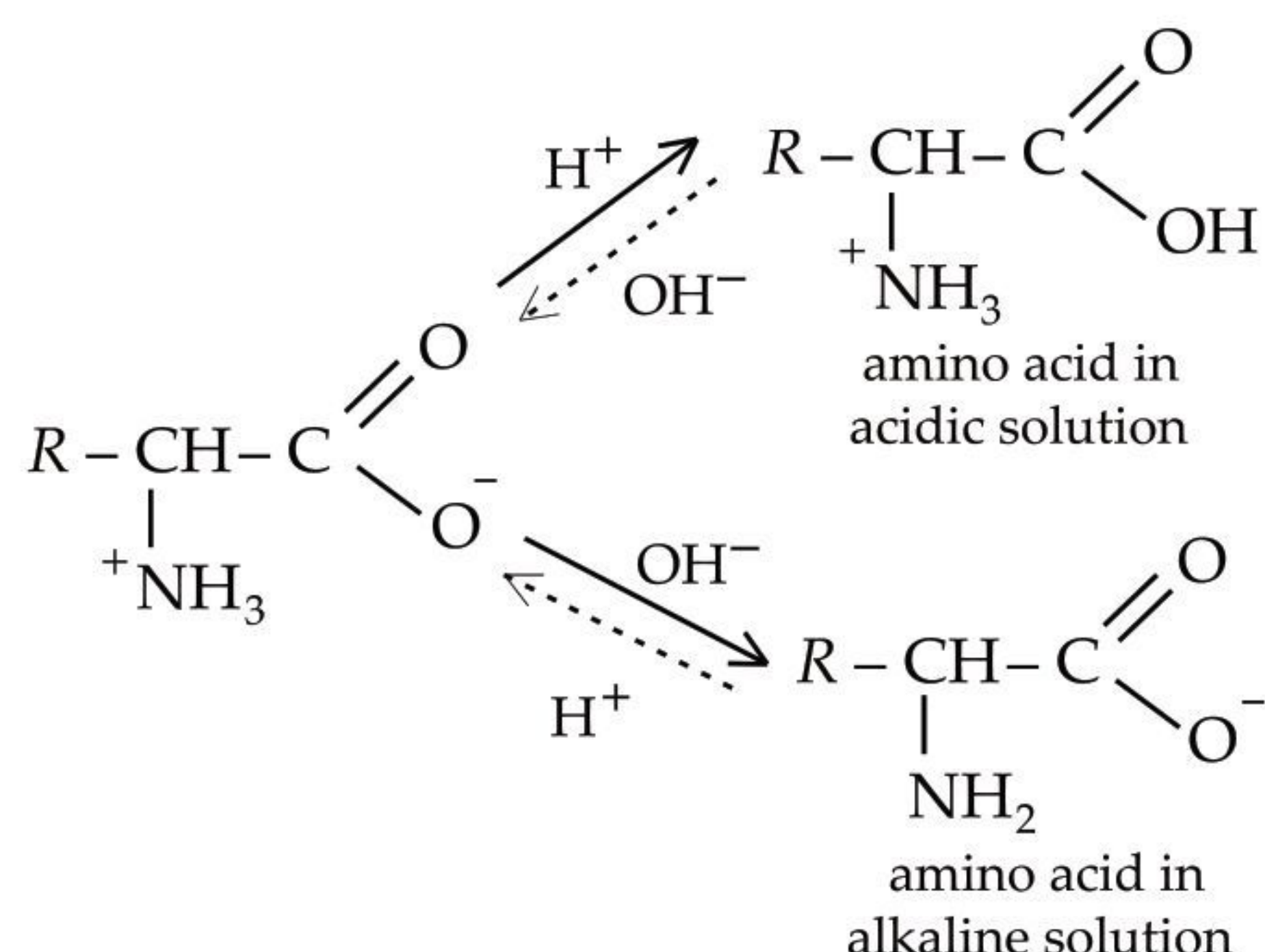
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Chemical Properties of α -Amino Acids

- These form salts with acids as well as with bases.



- Isoelectric point :** The pH at which dipolar ion (zwitter ion) exists as neutral ion, *i.e.*, it does not migrate to either electrode, is called isoelectric point. The amino acids have least solubility at isoelectric point which helps in their separation.
- Most naturally occurring amino acids have *L*-configuration.
- There are about 20 amino acids which make up the bioproteins. Out of these 10 amino acids (non-essential) are synthesised by our bodies and rest are essential in the diet (**essential amino acids**) and supplied to our bodies by food which we take because they cannot be synthesised in the body.

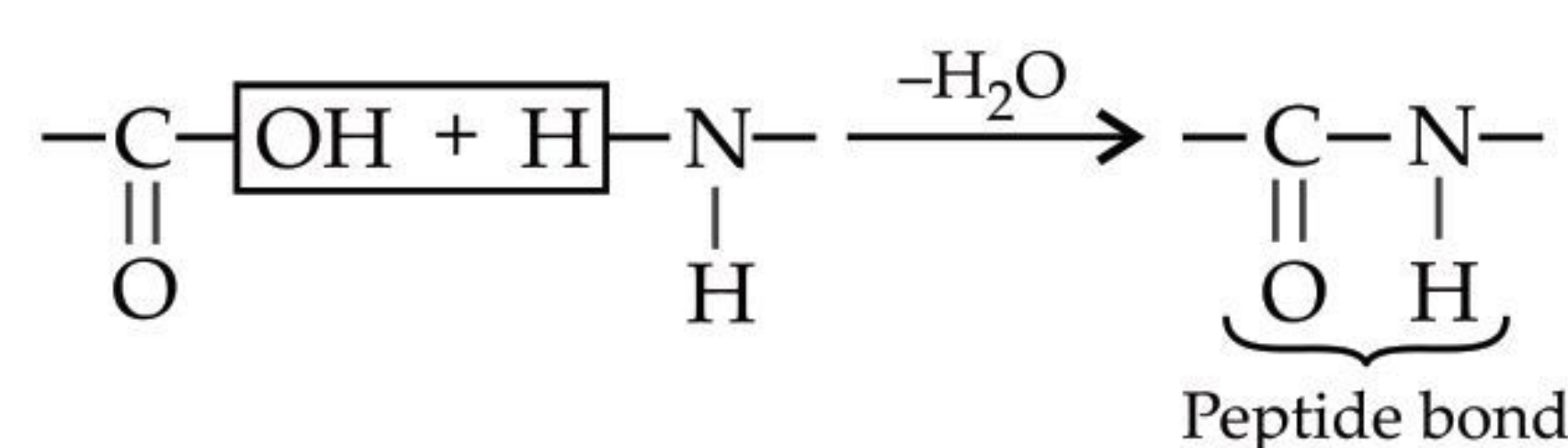
Name of amino acid		Structure of R	Three letter symbol
1	Glycine	—H	Gly
2	Alanine	—CH ₃	Ala
3	Valine*	—CH(CH ₃) ₂	Val
4	Leucine*	—CH ₂ CH(CH ₃) ₂	Leu
5	Isoleucine*	—CH(CH ₃)—CH ₂ CH ₃	Ile
6	Arginine*	—(CH ₂) ₃ NH—C(=NH)—NH ₂	Arg
7	Lysine*	—(CH ₂) ₄ NH ₂	Lys
8	Glutamic acid	—CH ₂ CH ₂ COOH	Glu
9	Aspartic acid	—CH ₂ COOH	Asp
10	Glutamine	—CH ₂ CH ₂ CONH ₂	Gln
11	Asparagine	—CH ₂ CONH ₂	Asn
12	Threonine*	—CHOH—CH ₃	Thr
13	Serine	—CH ₂ OH	Ser
14	Cysteine	—CH ₂ SH	Cys
15	Methionine*	—CH ₂ CH ₂ SCH ₃	Met

16	Phenylalanine*	—CH ₂ C ₆ H ₅	Phe
17	Tyrosine	—CH ₂ C ₆ H ₄ OH(<i>p</i>)	Tyr
18	Tryptophan*		Trp
19	Histidine*		His
20	Proline		Pro

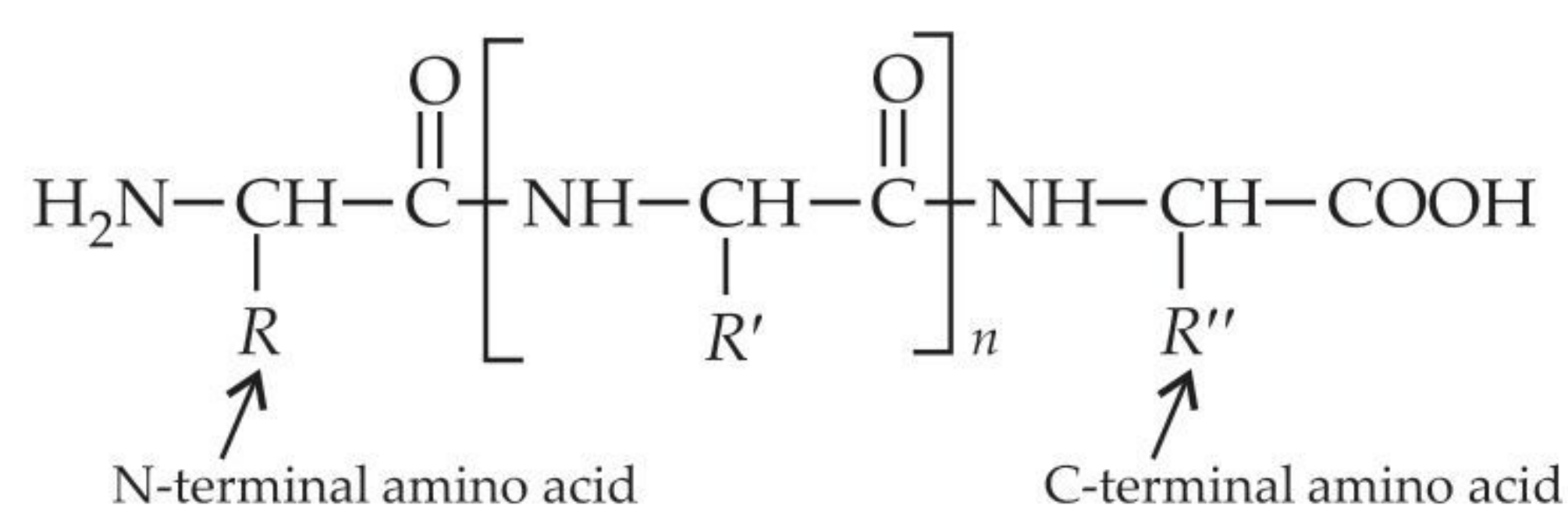
*Essential amino acids

Peptides

- Peptides are compounds formed by the condensation of two or more, same or different α -amino acids. When the amino acids condense, water molecules are eliminated, the resulting —CO—NH— linkage is called a peptide linkage or peptide bond.



- If a large number of α -amino acids are joined together by peptide bonds, the resulting polyamide is called a polypeptide.



Classification of Proteins

Fibrous proteins	In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, <i>e.g.</i> , keratin and myosin.
Globular proteins	Globular proteins result when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, <i>e.g.</i> , insulin and albumins.

Structure of Proteins

- Primary structure :** The covalent structure of a protein is called its *primary structure*.

- **Secondary structure :**

α -Helix	This is formed when the chain of α -amino acid coils as a right handed screw. Hydrogen bonding is responsible for holding helix in position. Such proteins are elastic.
β -Pleated sheet	Polypeptide chains are arranged side by side in a zig-zag manner. Neighbouring peptide chains are bonded together by intermolecular H-bonds in case, when R groups are smaller.

- **Tertiary structure :** Proteins often contain regions where a helical or sheet structure is folded up in a complex way to give a compact structure, known as the tertiary structure. *e.g.*: haemoglobin and myoglobin.
- **Quaternary structure :** Complex proteins formed from two or more α -helix structures are known as quaternary structures.

ENZYMES

- Enzymes are naturally occurring simple or conjugate proteins produced by living cells. Enzymes are biocatalysts which catalyse the

biochemical reactions in living organisms.

- Most active enzymes are associated with some non-protein components required for their activity. These are called prosthetic groups. The prosthetic group which is covalently attached with the enzyme molecule is known as cofactor.
- The prosthetic groups which get attached to the enzyme at the time of reaction are known as coenzymes.

Properties

- Have high efficiency and specificity.
- Required in very small quantities.
- Active at a temperature of 37°C and pH \approx 7.

HORMONES

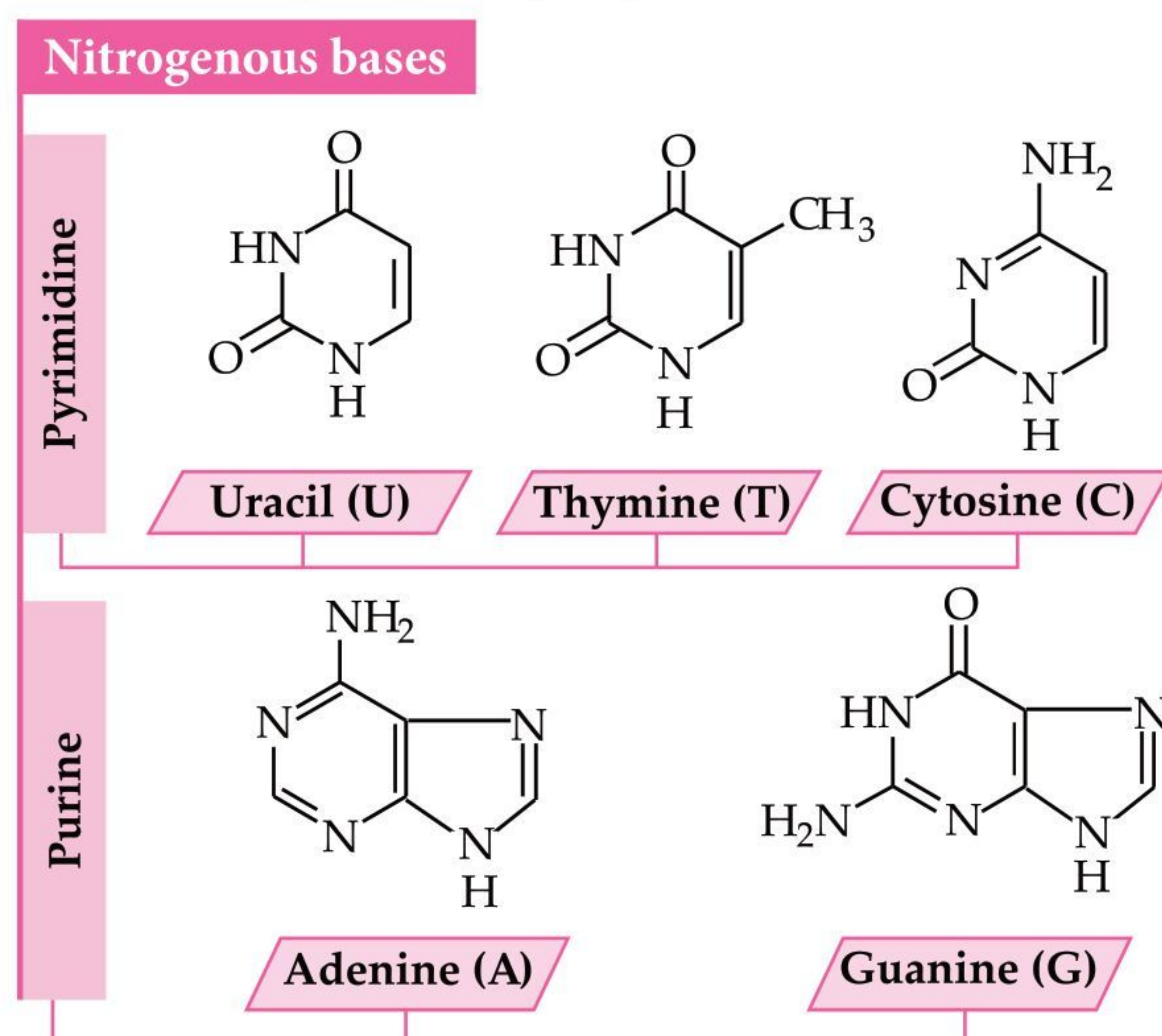
- Hormones are chemical substances that are produced in minute quantities by some specialised organs called ductless or endocrine glands. The hormones produced by these glands move to the different parts of the body through blood stream. Hormones play an important role in regulating metabolic processes and sex characteristics. Hormone deficiency leads to abnormal metabolic processes.

Hormones	Organ of secretion of hormone	Functions
1. Steroid hormones <ul style="list-style-type: none"> ● Androsterone and testosterone ● Estrone and estradiol ● Cortisone or Aldosterone 	Testes Ovary Adrenal cortex	It regulates the development and normal functioning of male sex organs. It regulates the development and normal functioning of female sex organs. It regulates the metabolism of carbohydrates, fats and mineral salts.
2. Peptide hormones <ul style="list-style-type: none"> ● Insulin ● Oxytocin ● Vasopressin 	Pancreas Posterior pituitary gland Posterior pituitary gland	It regulates the metabolism of glucose. It releases mother milk from mammary glands and controls the contraction of uterus after child birth. It controls the reabsorption of water in the kidney.
3. Amine hormones <ul style="list-style-type: none"> ● Thyroxine ● Adrenaline or epinephrine (also called emergency hormone) 	Thyroid gland Adrenal medulla	It controls the metabolism of proteins, carbohydrates and lipids. It releases glucose from glycogen and fatty acids from fats. It also increases the pulse rate and controls blood pressure.

NUCLEIC ACIDS

Nucleic acids are polynucleotides present in the nuclei of all living cells in the form of nucleoproteins.

- There are three basic components of each nucleotide monomeric unit, viz, pentose sugar, nitrogenous base and phosphate group.



- Nucleoside** : Pentose sugar + a nitrogenous base.
- Nucleotide** : Nucleoside + phosphoric acid (mainly at 5' carbon atom) or pentose sugar + nitrogenous base + phosphoric acid.

Types of Nucleic Acids

Components	Deoxyribonucleic Acid (DNA)	Ribonucleic Acid (RNA)
Sugar	D-(-)-2-deoxyribose	D-(-)ribose
Pyrimidine base	Cytosine and thymine	Uracil and cytosine
Purine base	Adenine and guanine	Adenine and guanine
Phosphoric acid	H ₃ PO ₄	H ₃ PO ₄
Structure	Double stranded α -helix	Single stranded α -helix
Replication	Possible	Not possible

- Chargaff's rule** : The rule describes base composition of a DNA molecule.
 - It states that amount of purine bases is always equal to that of pyrimidine bases.
 - Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand.

- Adenine (A) pairs with thymine (T) through two H-bonds ($A = T$) and guanine (G) pairs with cytosine (C) through three H-bonds ($G \equiv C$).
- In case of RNA, adenine (A) pairs with uracil (U), ($A = U$).

Biological Functions of Nucleic Acids

- Replication** : It is the enzyme catalysed process by which a single DNA molecule produces two identical copies of itself.
- Protein synthesis** : It is carried out by RNA molecules in two steps :
 - Transcription** : It is the process of synthesis of RNA from DNA in the cytoplasm of the cell.
 - Translation** : The *m*-RNA directs the protein synthesis by this process.
- Genetic code** : Linear sequences of three nucleotides (triplets) in DNA or RNA that determines the specific amino acid sequence in the synthesis of proteins is called genetic code. It is the biochemical basis of heredity and nearly universal in all organisms.
- Mutation** : It is a change in nitrogenous base sequence of DNA molecule which leads to the synthesis of proteins with an altered sequence of amino acids. Mutation may cause genetic disorders or diseases.

VITAMINS

- Vitamins** are organic compounds other than carbohydrates, proteins, fats or a group of biomolecules, which must be supplied in small amounts in diet for maintaining a normal health, growth and nutrition.
- Multiple deficiencies caused by lack of more than one vitamins is known as **avitaminosis**.

Classification

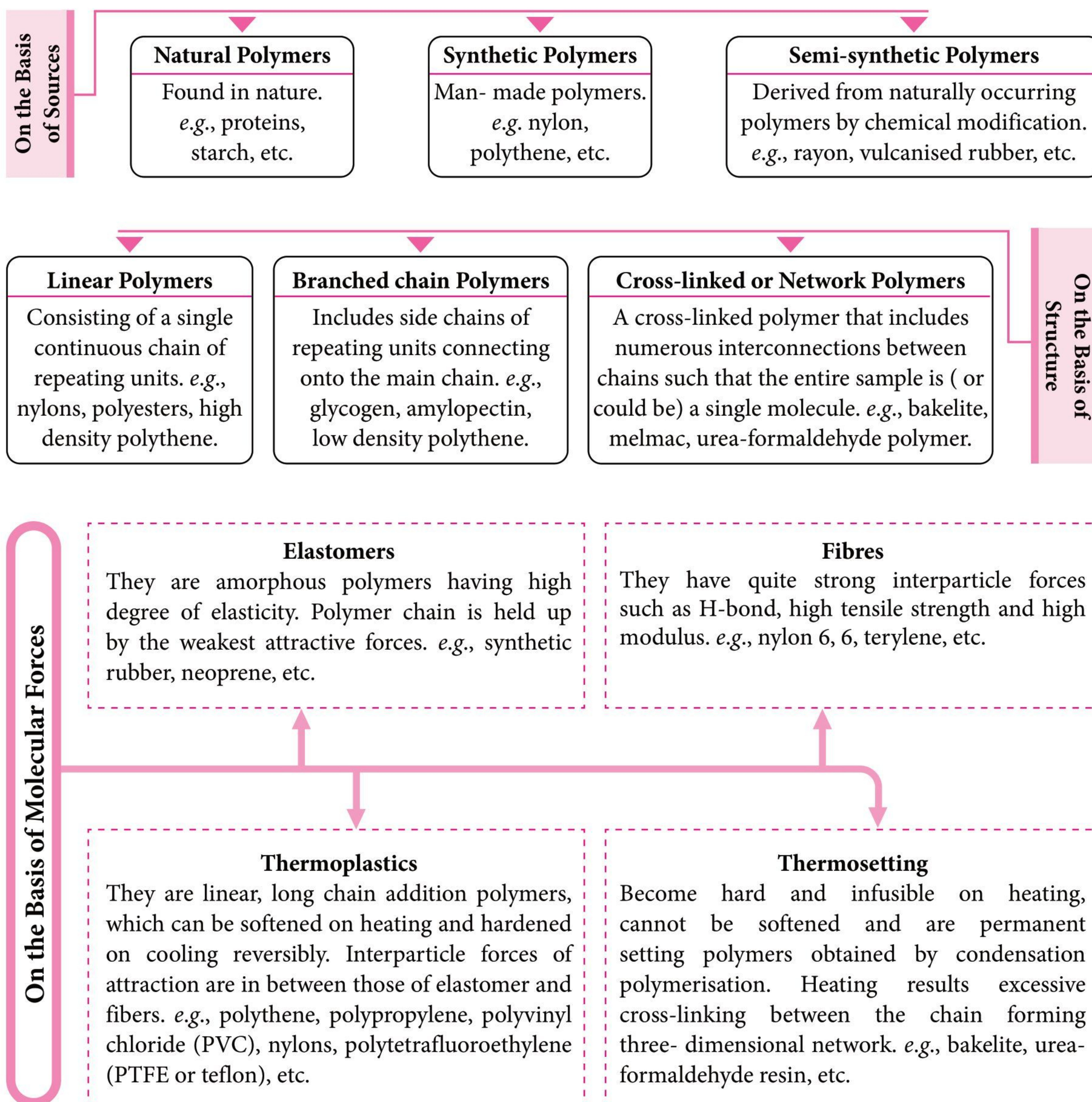
- Vitamins are generally classified into two broad categories :
 - Water soluble vitamins**: Those vitamins which are soluble in water are called water soluble vitamins, e.g., vitamins B group, vitamin C, etc.
 - Fat soluble vitamins**: Those vitamins which are soluble in fats are called fat soluble vitamins, e.g., vitamins A, D, E and K. Excess intake of these vitamins may cause hypervitaminosis.

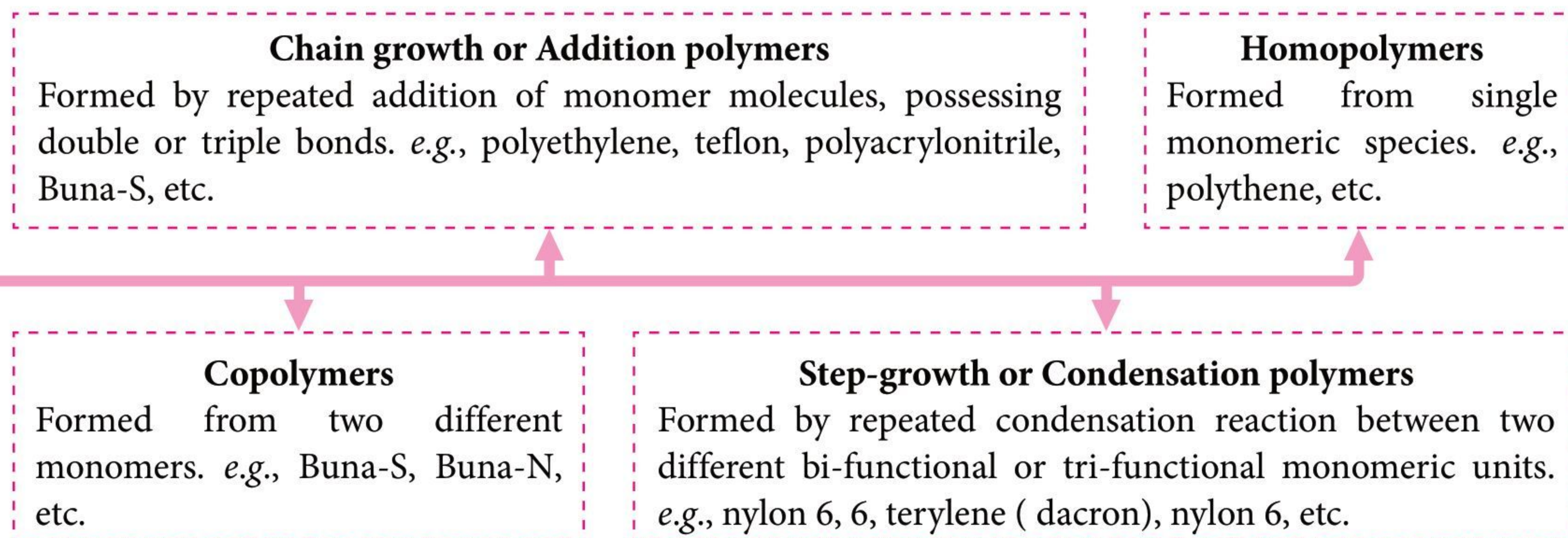
Polymers

INTRODUCTION

- A polymer is a naturally occurring or synthetic macromolecule made up of a linked series of a large number of repeated simple molecules, called monomers.
- Naturally occurring polymers are proteins, starch, cellulose, rubber and DNA. Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses *e.g.*, plastics.

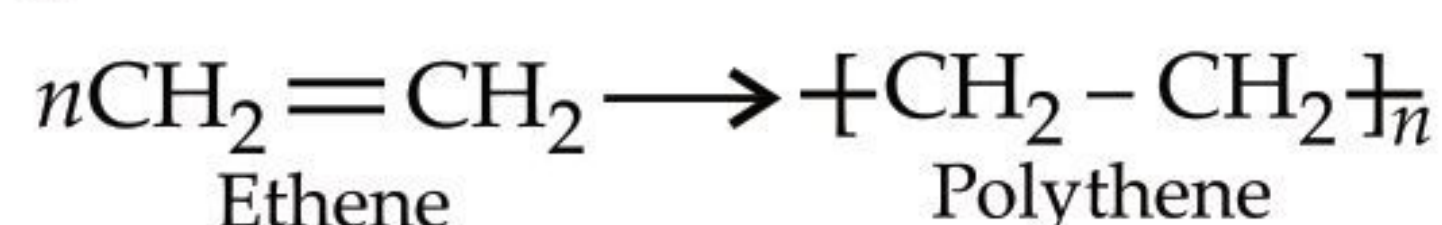
Classification of Polymers





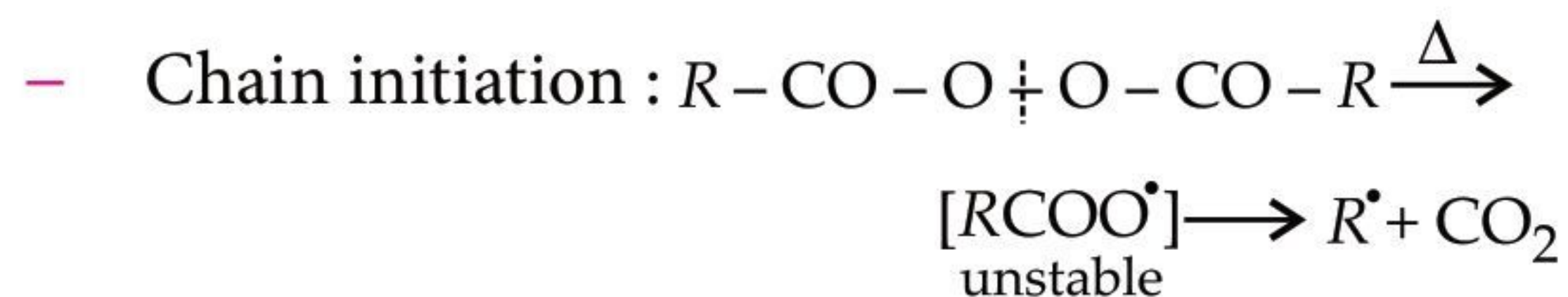
Methods of Polymerisation

- Addition or chain growth polymerisation :** A polymer formed by direct addition of repeated monomers without the elimination of byproduct molecules is called addition polymer and the phenomenon is known as addition polymerisation.

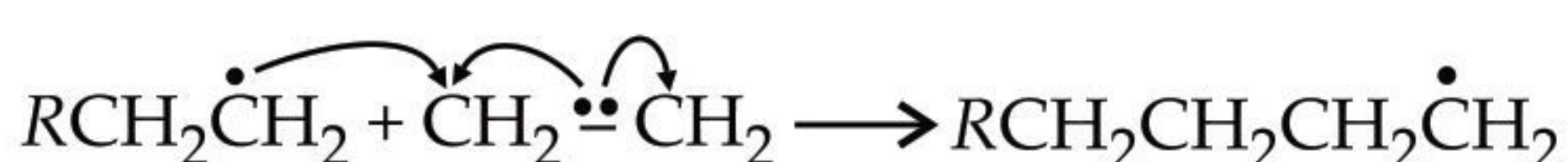
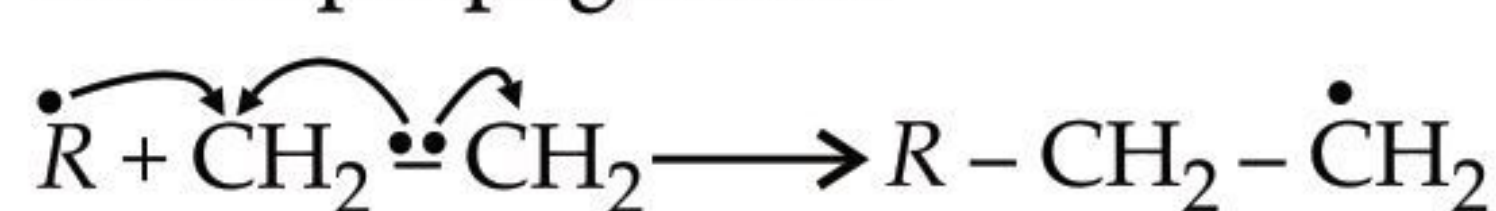


Chain growth polymerisation follows two basic mechanisms :

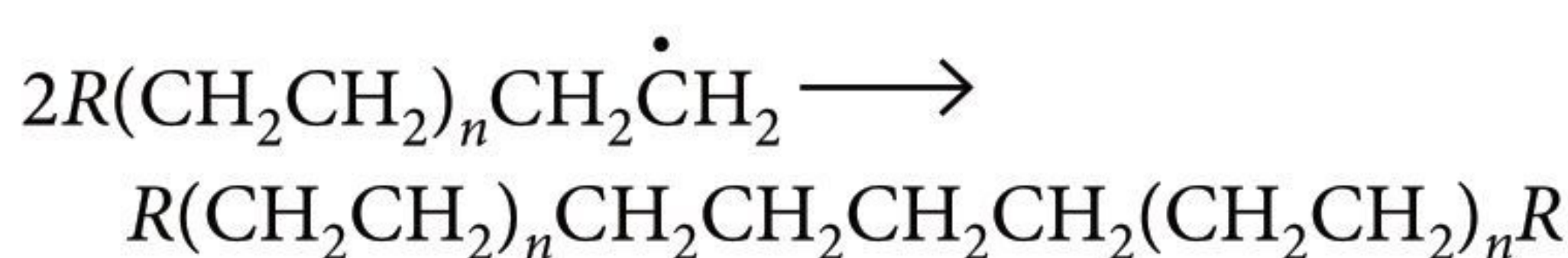
- Free-radical mechanism :**



- Chain propagation :

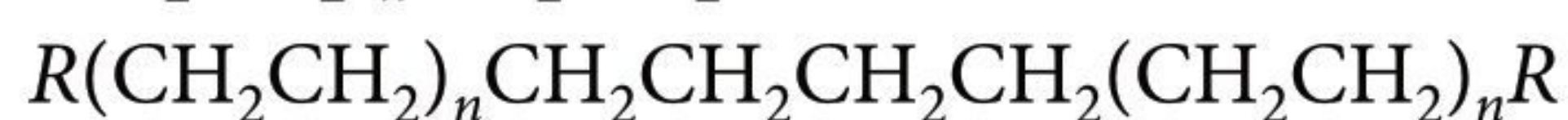
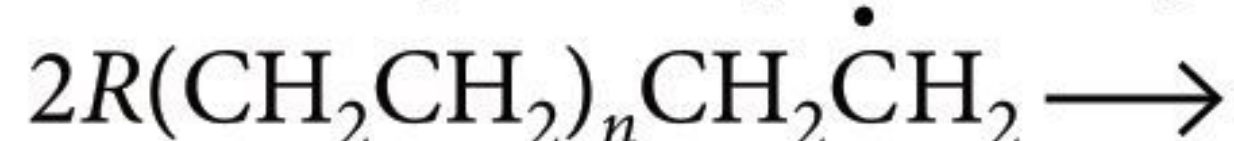
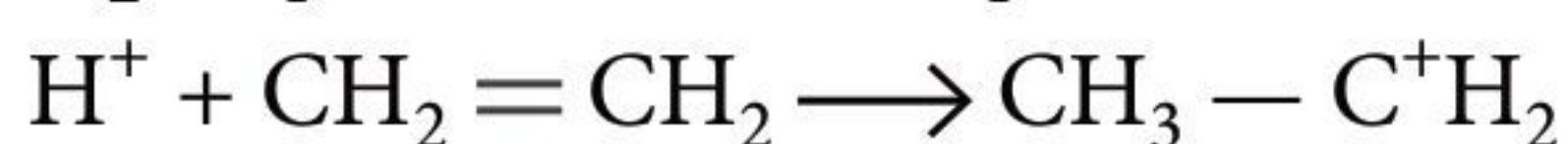
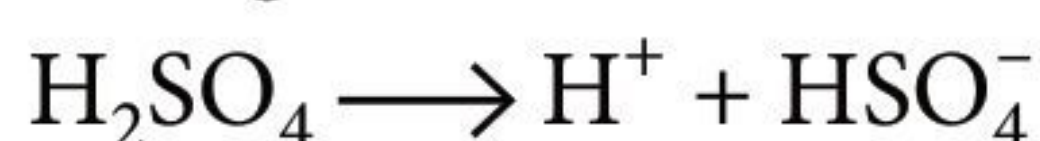


- Chain termination :



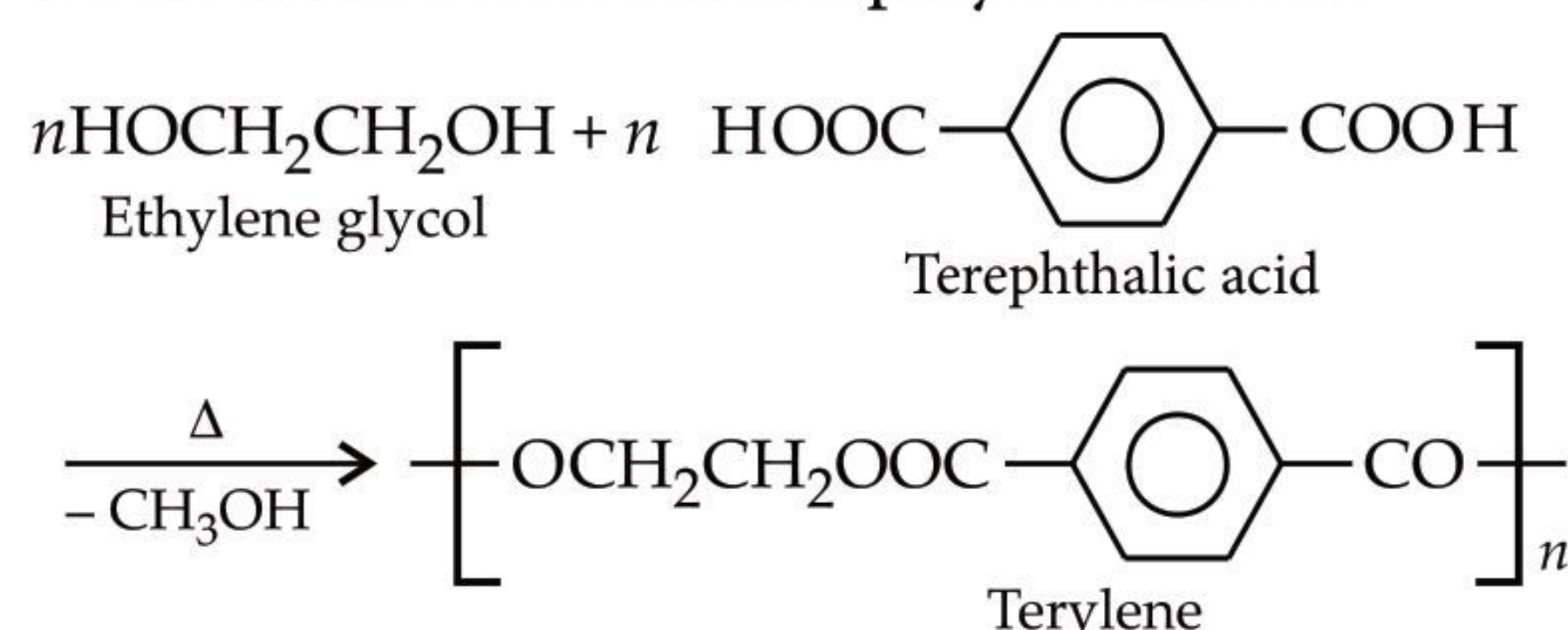
- Ionic mechanism :**

(a) **Cationic mechanism** initiated by the use of strong Lewis acids such as HF, AlCl₃, H₂SO₄, etc.

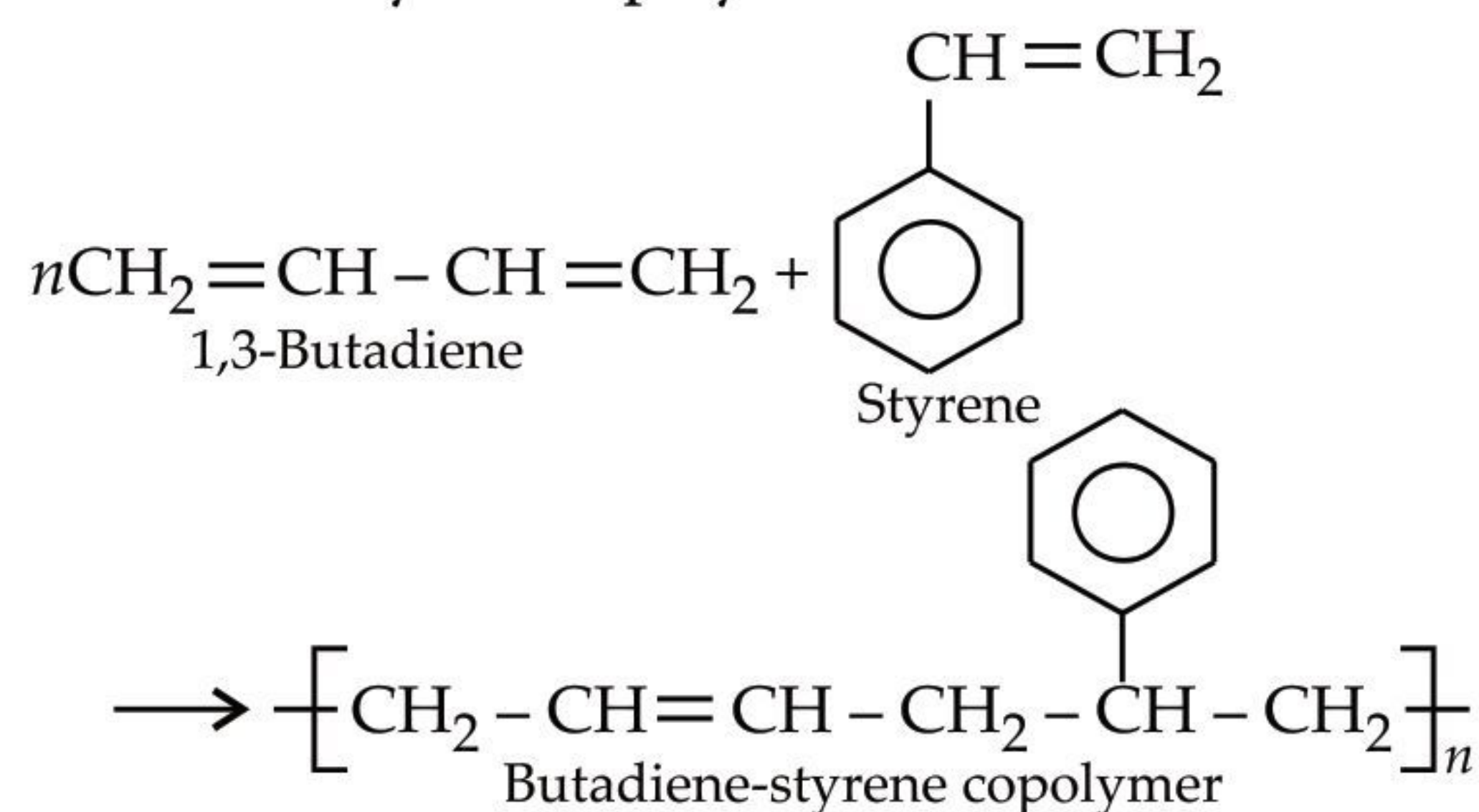


(b) **Anionic mechanism** occurs in alkenes having electron withdrawing groups in them and it is carried out in presence of a suitable base.

- Condensation or step growth polymerisation :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc. is called condensation polymer and the phenomenon is known as condensation polymerisation.



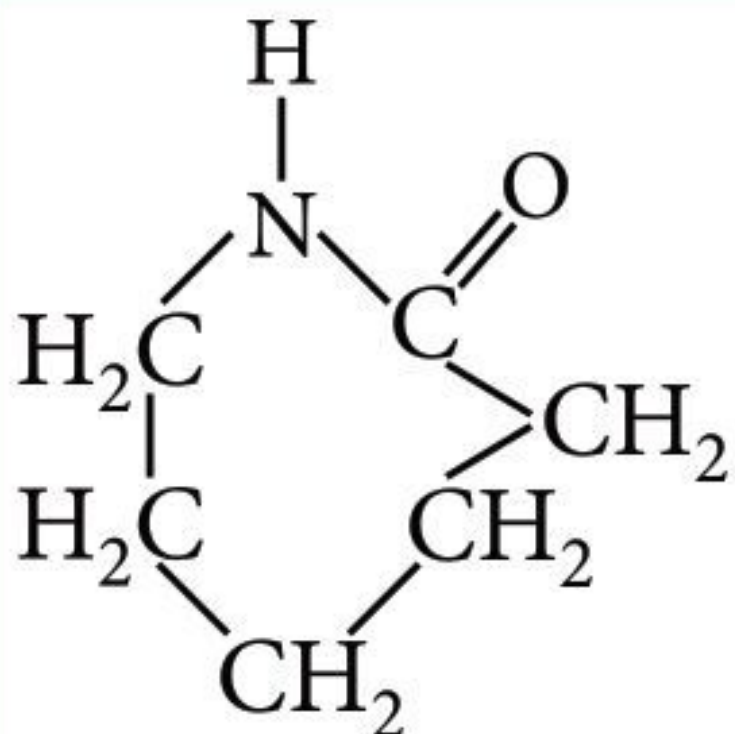
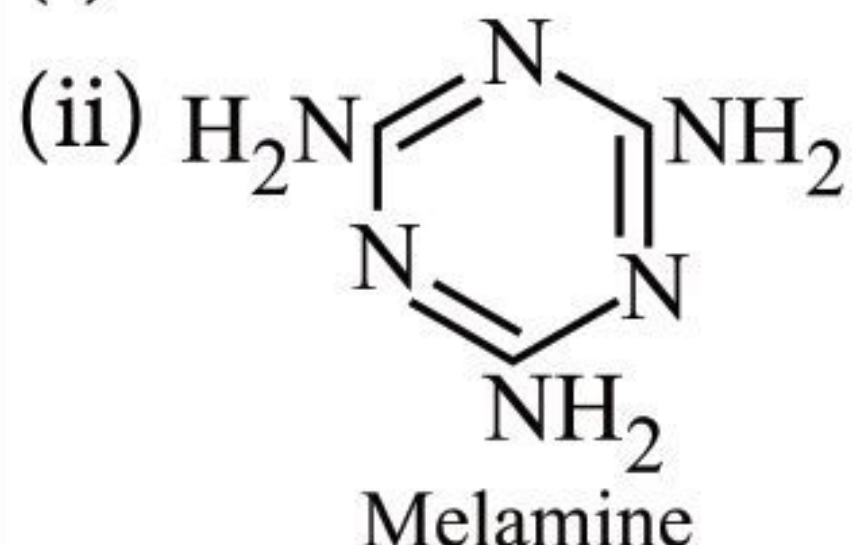
- Copolymerisation :** A polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise to form a copolymer is called copolymerisation. Copolymers can be prepared by both chain growth and step growth polymerisation, *e.g.*, Butadiene-styrene copolymer.



MONTHLY TEST DRIVE CLASS XII ANSWER KEY

1. (b)	2. (c)	3. (c)	4. (d)	5. (b)
6. (b)	7. (b)	8. (b)	9. (a)	10. (d)
11. (b)	12. (d)	13. (b)	14. (c)	15. (d)
16. (a)	17. (d)	18. (a)	19. (a)	20. (b, c)
21. (c, d)	22. (a, c)	23. (b, c, d)	24. (241.5)	25. (0.717)
26. (9)	27. (b)	28. (b)	29. (a)	30. (c)

Some Commercially Important Polymers

Homopolymers			
	Common name	Monomer	Uses
1.	Polyethylene	$\text{CH}_2 = \text{CH}_2$ Ethylene	In the manufacture of pipes, toys, bags, wires, insulators, bottles, etc.
2.	Polyvinyl chloride (PVC)	$\text{CH}_2 = \text{CHCl}$ Vinyl chloride	In the manufacture of sheets, water pipes, hoses, hand bags, etc.
3.	Polystyrene	$\text{C}_6\text{H}_5\text{CH} = \text{CH}_2$ Styrene	In the manufacture of combs, toys, radio and television cabinets, etc.
4.	Polyacrylonitrile (PAN)	$\text{CH}_2 = \text{CH} - \text{CN}$ Acrylonitrile	In the manufacture of orlon (fibre) and acrilon films.
5.	Teflon (Polytetrafluoroethylene)	$\text{CF}_2 = \text{CF}_2$ Tetrafluoroethylene	In the manufacture of insulators, gaskets, etc.
6.	Nylon-6		In making tyre cords, ropes, fishing nets, toys, etc.
Copolymers			
	Common name	Monomers	Uses
1.	Dacron or Terylene	(i) $\text{HOCH}_2 - \text{CH}_2\text{OH}$ Ethylene glycol (ii) $\text{HOOC} - \text{C}_6\text{H}_4 - \text{COOH}$ Terephthalic acid	In the manufacture of fabrics and magnetic recording tapes.
2.	Nylon-6,6	(i) $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ Hexamethylene diamine (ii) $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ Adipic acid	In the manufacture of sheets, bristles of brushes and textiles.
3.	Bakelite	(i) HCHO Formaldehyde (ii) $\text{C}_6\text{H}_5\text{OH}$ Phenol	In the manufacture of electrical goods, phonograph records, fountain pen barrels, combs, etc.
4.	Melamine - formaldehyde resin	(i) HCHO Formaldehyde (ii)  Melamine	In the manufacture of plastic crockery

RUBBER

• Natural rubber :

- It is obtained as latex from rubber tree.
- It is *cis*-1,4-polyisoprene.
- All *trans* configuration occurs naturally as *gutta-percha*, which is non-elastic.

• Synthetic rubber :

- It is obtained by polymerizing certain organic compounds which may have properties similar to rubber and some additional desirable

properties.

- **Neoprene or polychloroprene** : Prepared by free radical polymerisation of chloroprene in presence of O_2 or peroxides.
- Greater stability to aerial oxidation and in its resistance to action of vegetables or mineral oils.
- **Buna-S** : Prepared by free radical copolymerisation 1, 3-butadiene with styrene. It is very tough, possesses high abrasion resistance, high load bearing capacity.

- **Buna-N** : Prepared by copolymerisation of 1, 3-butadiene with acrylonitrile in presence of a peroxide catalyst.
- **Thiokol** : Prepared by copolymerisation of ethylene dichloride with sodium tetrasulphide in presence of magnesium hydroxide.
- **Vulcanization of rubber** : It is a process of treating natural rubber with sulphur and an appropriate additive at a temperature range of 373 to 415 K, to modify its properties.
 - On vulcanization sulphur forms cross-links at the reactive sites of the double bonds and gives mechanical strength to the rubber.
 - The extent of hardness or toughness, however, depends upon the amount of sulphur added. Thus, about 5% sulphur is used for making tyre rubber, 20-25% sulphur for making ebonite and 30% sulphur for making battery case rubber.

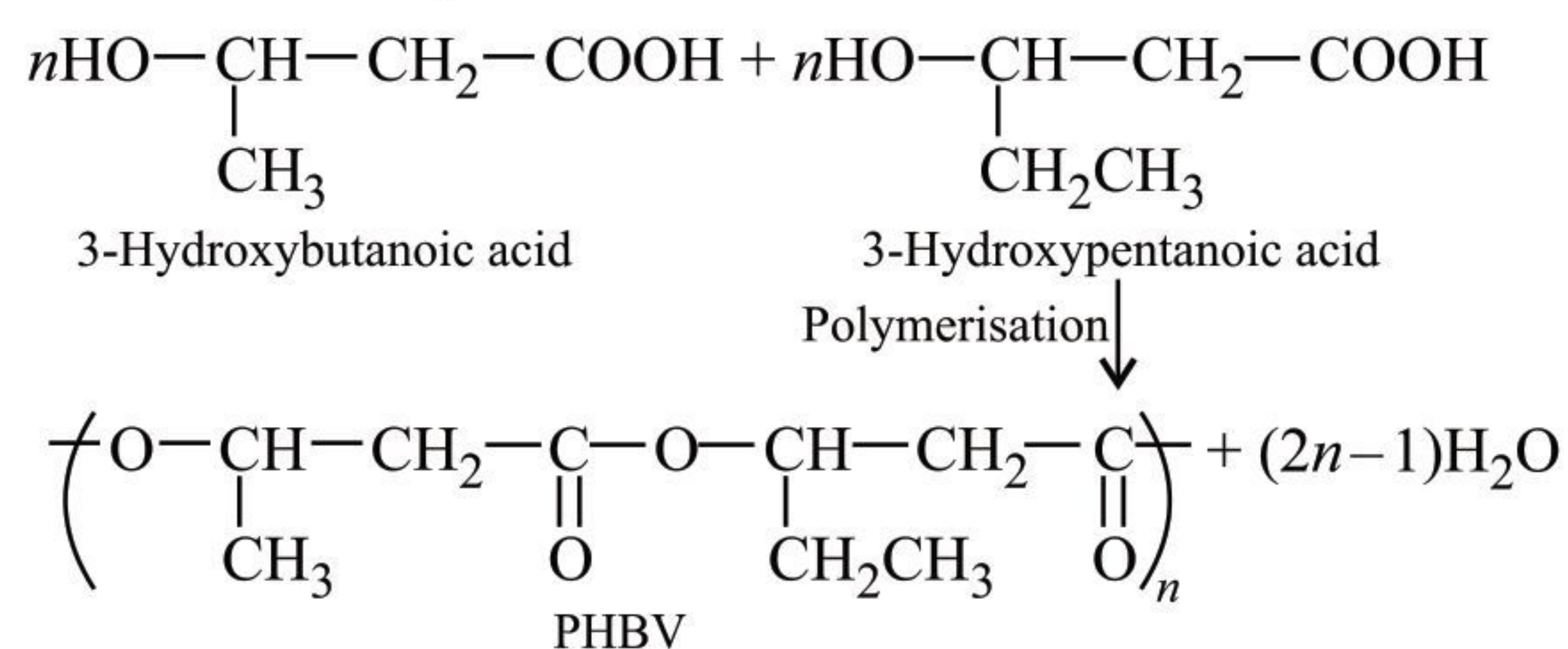
POLYTHENE

- **High density polythene** :
 - Obtained by heating ethylene at 333 K to 343 K and 6-7 atm.
 - Linear molecules and closely packed.
 - High density (0.97 g/cm³) and high melting point (403 K) and quite harder, greater tensile strength.
 - Used for manufacturing containers, housewares, pipes, etc.
- **Low density polythene** :
 - Obtained by heating ethylene under high pressure (1000-2000 atm) at temperature of 350 to 570 K in presence of traces of oxygen or peroxide initiator.
 - Formed by free radical addition polymerisation.
 - Highly branched chain molecules.
 - Low density (0.92 g/cm³), low melting point (384 K) and is chemically inert and tough.
 - Used for packaging, insulation and manufacturing pipes, toys, etc.

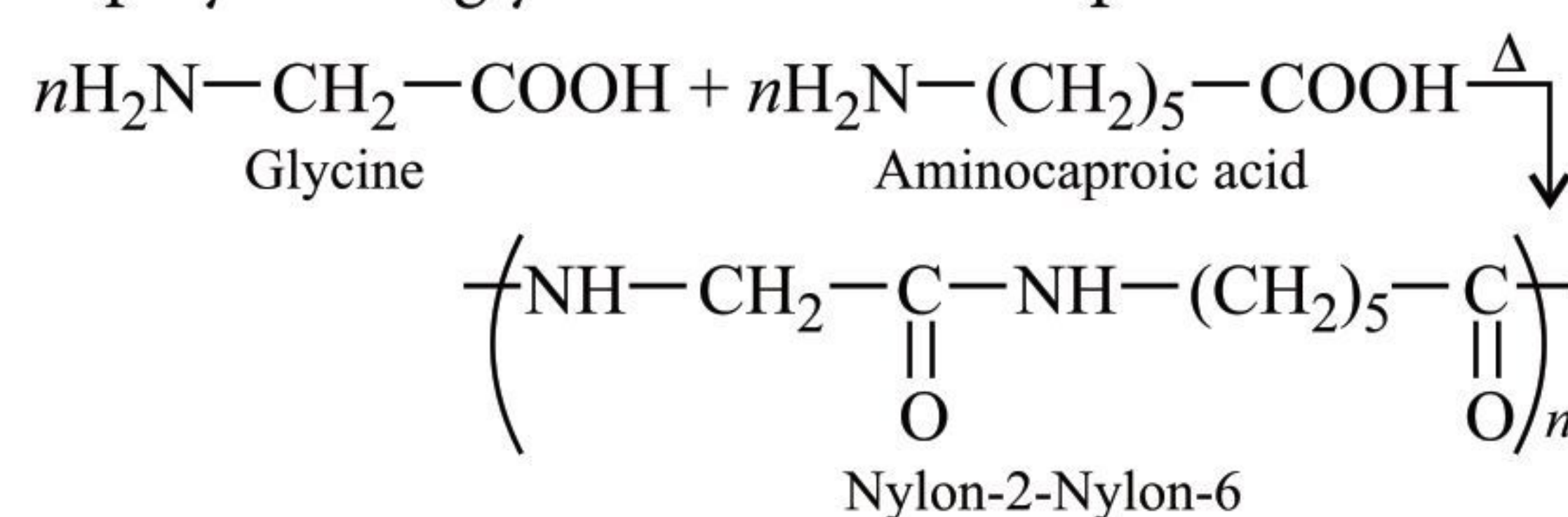
Biodegradable Polymers

- Biopolymers disintegrate by enzymatic hydrolysis and to some extent by oxidation and hence are biodegradable.

- **Poly-β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV)** : It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid connected with ester linkages.



- Used in speciality packaging, orthopaedic devices and in controlled drug release.
- **Dextran** : A copolymer of glycolic acid and lactic acid (90 : 10) was the first biodegradable polyester used for stitching of wounds.
- **Nylon-2-Nylon-6** : It is a step-growth polyamide copolymer of glycine and amino caproic acid.



MOLECULAR MASS OF POLYMERS

- Polymers contain chains of various lengths and therefore, their molecular mass is always expressed as an average. However natural polymers have definite length and definite molecular mass.
- It is expressed in two ways :
 - **Number average molecular mass (\bar{M}_N)** is

$$\text{defined as } \bar{M}_N = \frac{\sum N_i M_i}{\sum N_i}$$

Where, N_i is the number of molecules of the i^{th} type with molecular mass M_i .

- **Weight average molecular mass (\bar{M}_w)** is defined as

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Where N_i is the number of molecules of mass M_i .

- Polydispersity Index : $\text{PDI} = \frac{\bar{M}_w}{\bar{M}_N}$

- There is no aspect of our life that is not affected by the developments in chemistry, infact chemistry plays a very important role in our everyday life.

CHEMICALS IN MEDICINES

- Drugs are low molecular mass (~100 – 500 u) chemicals which interact with macromolecular targets and produce a biological response. When the biological response is therapeutic and useful, these chemicals are called medicines.
- **Classification of drugs** : Drugs are classified on the basis of
 - **Drug action** : It is based on the action of a drug on a particular biochemical process *e.g.*, Antihistamines
 - **Chemical structure** : It is based on the chemical structure of the drug *e.g.*, Sulphonamides
 - **Pharmacological effect** : Analgesics (pain killers), antiseptics (kill or arrest the growth of microorganisms), Antipyretics(reduce fever)
 - **Molecular targets** : It is based on the interaction with biomolecules such as carbohydrates, lipids, proteins and nucleic acids.

Drug Target Interaction

- **Enzymes as drug target** : Drugs either can block the binding site of the enzyme and prevent the binding of substrate or they can inhibit the catalytic activity of enzyme.
- **Receptors as drug target** : Proteins which transmit communication to the different parts of the body are called **receptors**. Receptor proteins are embedded in the cell membrane and receptor changes its shape to accommodate a chemical messenger which brings about transfer of message into the cell.
- **Drug interact with receptors in two ways** :
 - Drugs bind to their receptor sites and inhibit its natural function (antagonists). These are useful when blocking of message is required.
 - Some drugs mimic the natural messenger by switching on the receptor (agonists). These are useful when there is lack of natural chemical messenger.

Therapeutic Action of Different Classes of Drugs

- **Sulpha Drugs** : Derivatives of sulphanilamide, widely used in curing bacterial infections.
- **Antipyretics** : Reduce body temperature in high fever.
- **Analgesics** : Reduce pain, mainly of two types
 - **Non-narcotic analgesics** : *e.g.*, Aspirin (anti-coagulant) and paracetamol.
 - **Narcotic analgesics** : *e.g.*, Morphine and its homologues (pain-relieving and sleep producing)
- **Antacids** : Neutralize excess acid in the gastric juices and give relief from acid indigestion, heart burns and gastric ulcers, *e.g.*, magnesium hydroxide, calcium carbonate, etc.
- **Antihistamines** : Prevent allergic reactions *e.g.*, diphenylhydramine(benadryl), pheniramine maleate (avil), etc.
- **Antimicrobials** : Destroys or inhibits the growth of pathogens, can be classified as antiseptic, disinfectants and antibiotics etc.
- **Antiseptics and disinfectants** : The chemical substances which are used to either kill or prevent the growth of microorganisms on skin surfaces and living tissues are called *antiseptics*. While the chemical substances which are used to kill microorganisms on inanimate objects are called *disinfectants*.
 - The same substance can act as disinfectant as well as antiseptic depending upon its concentration. For example, a 0.2% solution of phenol acts as antiseptic and its 1% solution acts as disinfectant.
 - Dettol is a mixture of chloroxylenol and terpenol in a suitable solvent.
 - Iodine is a powerful antiseptic. It is used as a tincture of iodine which is 2-3% iodine solution of alcohol-water.
- **Antibiotics** : Chemical substances produced wholly or partly by chemical synthesis which in low concentration inhibit the growth or destroy micro-organisms by intervening in their metabolic processes.

- The antibiotics may be either **bactericidal** (kill the organisms in the body) *e.g.*, penicillin, ofloxacin, etc., or **bacteriostatic** (inhibit the growth of organisms), *e.g.*, erythromycin, chloramphenicol, etc.
- Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics, *e.g.*, tetracycline, chloromycetin and chloramphenicol.
- Those effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics, *e.g.*, penicillin-G.
- **Tranquilizers** : Chemical substances are used for the treatment of stress, mild and severe mental diseases.
- Tranquilizers can be classified as :
 - **Narcotics** : Analgesic and depressant. *e.g.*, pethidine, heroin, opium etc.
 - **Hypnotics** : Tranquilizers, used to reduce anxiety and mental tension.
 - **Sedatives** : Induces the feeling of relaxation, calmness and drowsiness. *e.g.*, Valium, barbiturates .
 - **Antidepressants** : Mood boosters, induces the feeling of well being. *e.g.*, methedrine and cocaine.
- **Antifertility Drugs** : Oral contraceptives, progesterone either alone or in combination with estrogen and steroids, controls pregnancy. *e.g.*, mifepristone, ethynylestradiol, etc.

CHEMICALS IN FOOD

- **Preservatives** : Chemical substances which are added to the food material to prevent their spoilage, retain their nutritive value for long periods and prevent the rancidity of food *e.g.*, sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$).
- **Artificial Sweetening Agents** : Chemical compounds which give sweetening effect to the food and enhance its odour and flavour.

Artificial sweetener	Sweetness value in comparison to cane sugar
Aspartame	100
Sucralose	600
Alitame	2000

- **Antioxidants** : Chemical substances which prevent oxidation and subsequent spoilage of the food.

CLEANSING AGENTS

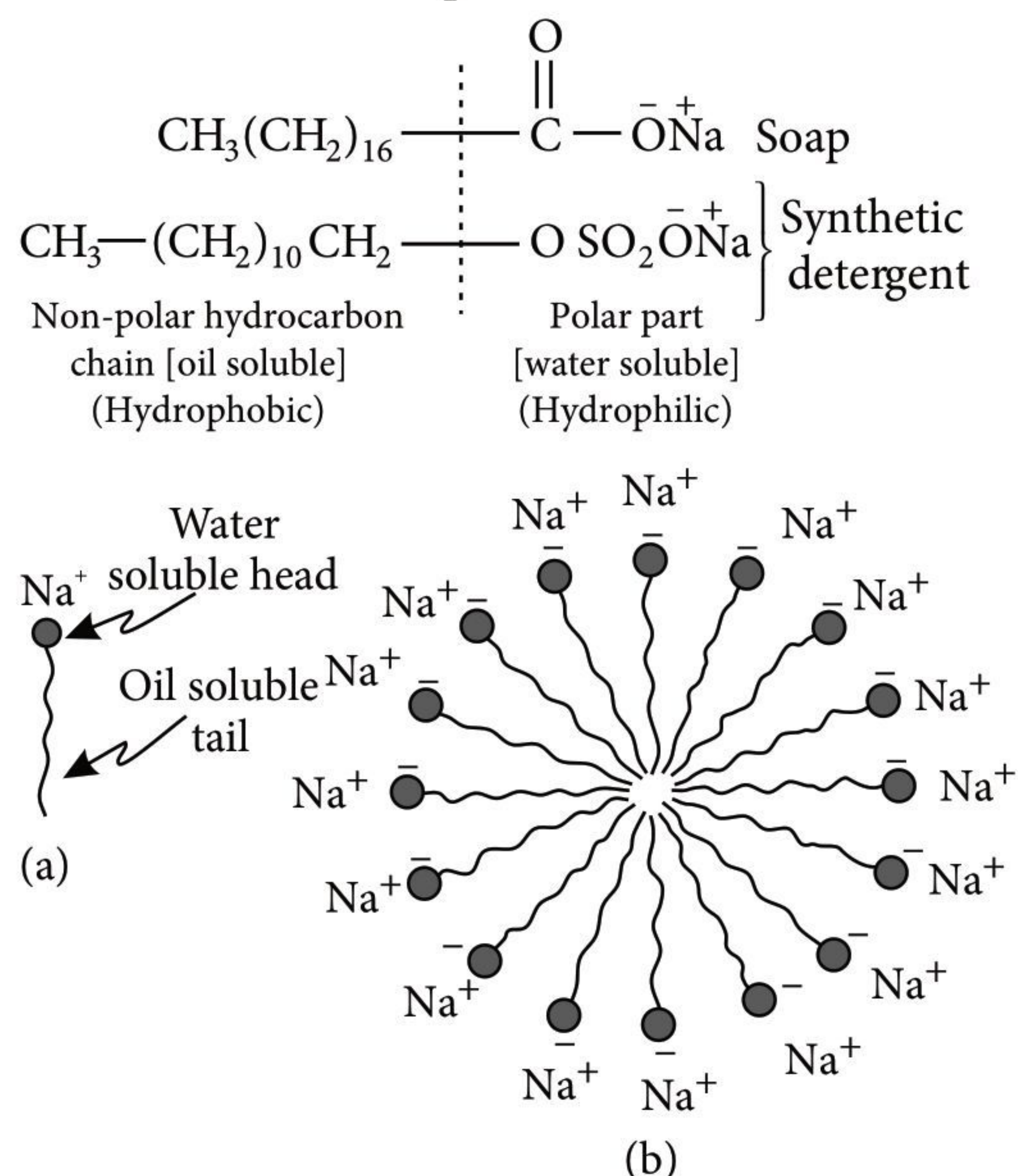
- **Soaps** : Sodium or potassium salts of higher fatty acids (with 12-18 carbon atoms) *e.g.*, salts of $\text{C}_{15}\text{H}_{31}\text{COOH}$ (palmitic acid), $\text{C}_{17}\text{H}_{35}\text{COOH}$ (stearic acid), $\text{C}_{17}\text{H}_{33}\text{COOH}$ (oleic acid), $\text{C}_{17}\text{H}_{31}\text{COOH}$ (linoleic acid), etc.
- **Soapless soaps or synthetic detergents** : Sodium salts of long chain alkyl hydrogen sulphates or the sodium salts of long chain benzene sulphonic acids.
- **Cationic detergents** : Quaternary ammonium salts of amines with acetates or halides as anions. *e.g.*, trimethylstearyl ammonium chloride, $\text{CH}_3(\text{CH}_2)_{17}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$
- **Anionic detergents** : Anionic hydrophilic groups *e.g.*, sodium lauryl sulphate, $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$
- **Non-ionic detergents** : Esters of high molecular mass and do not contain ions *e.g.*, polyethyleneglycol stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{OH}$

Cleansing Action of Soaps and Detergents

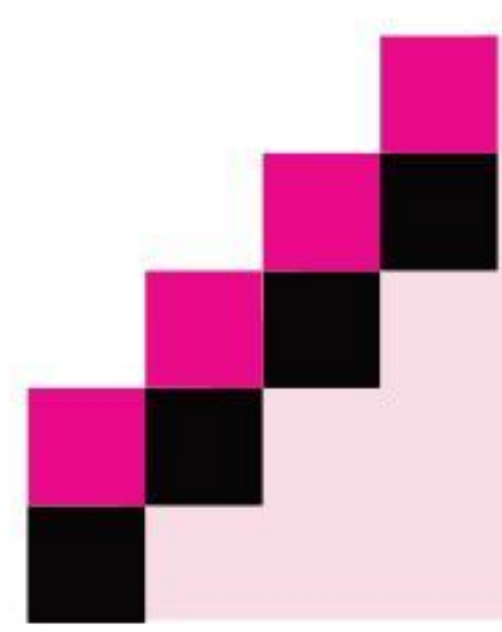
- The hydrocarbon chains of soaps or detergent molecules cluster together forming structure called *micelles*.

In the micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere.

Being negatively charged, soap micelles repel each other and remain dispersed in water.



(a) A soap molecule (b) Emulsified grease globule



WRAP it up!

MCQs Type

1. Drugs are classified on the basis of
(i) chemical structures
(ii) pharmacological effects
(iii) molecular targets (iv) action of drugs.
Correct answer is
(a) only (iii) (b) only (ii) and (iv)
(c) only (i) and (iii) (d) all of these.
2. Cleansing action of cationic detergent is due to
(a) hydrophobic part of cation
(b) hydrophilic part of cation
(c) hydrophobic part of anion
(d) hydrophilic part of anion.

3. Match List I with List-II.

List-I	List-II
(A) Chloroprene	(i)
(B) Neoprene	(ii)
(C) Acrylonitrile	(iii)
(D) Isoprene	(iv) $\text{CH}_2 = \text{CH} - \text{CN}$

(JEE Main 2020)

Choose the correct answer from the options given below.

- (a) (A) – (iii), (B) – (iv), (C) – (ii), (D) – (i)
(b) (A) – (ii), (B) – (i), (C) – (iv), (D) – (iii)
(c) (A) – (iii), (B) – (i), (C) – (iv), (D) – (ii)
(d) (A) – (ii), (B) – (iii), (C) – (iv), (D) – (i)
4. Cane sugar on hydrolysis gives
(a) glucose and galactose
(b) glucose and fructose
(c) glucose only (d) fructose only.
5. Starch can be used as an indicator for the detection of the traces of
(a) glucose in aqueous solution
(b) proteins in blood
(c) iodine in aqueous solution
(d) urea in blood.

6. The secondary structure of a protein refers to
(a) fixed configuration of the polypeptide backbone
(b) α -helical backbone
(c) hydrophobic interactions
(d) sequence of α -amino acids.
7. Two samples of DNA, A and B have melting points 340 K and 350 K respectively. This is because
(a) B has more GC content than A
(b) A has more GC content than B
(c) B has more AT content than A
(d) both have same AT content.
8. The RBC deficiency is deficiency disease of
(a) vitamin B₂ (b) vitamin B₁₂
(c) vitamin B₆ (d) vitamin B₁.

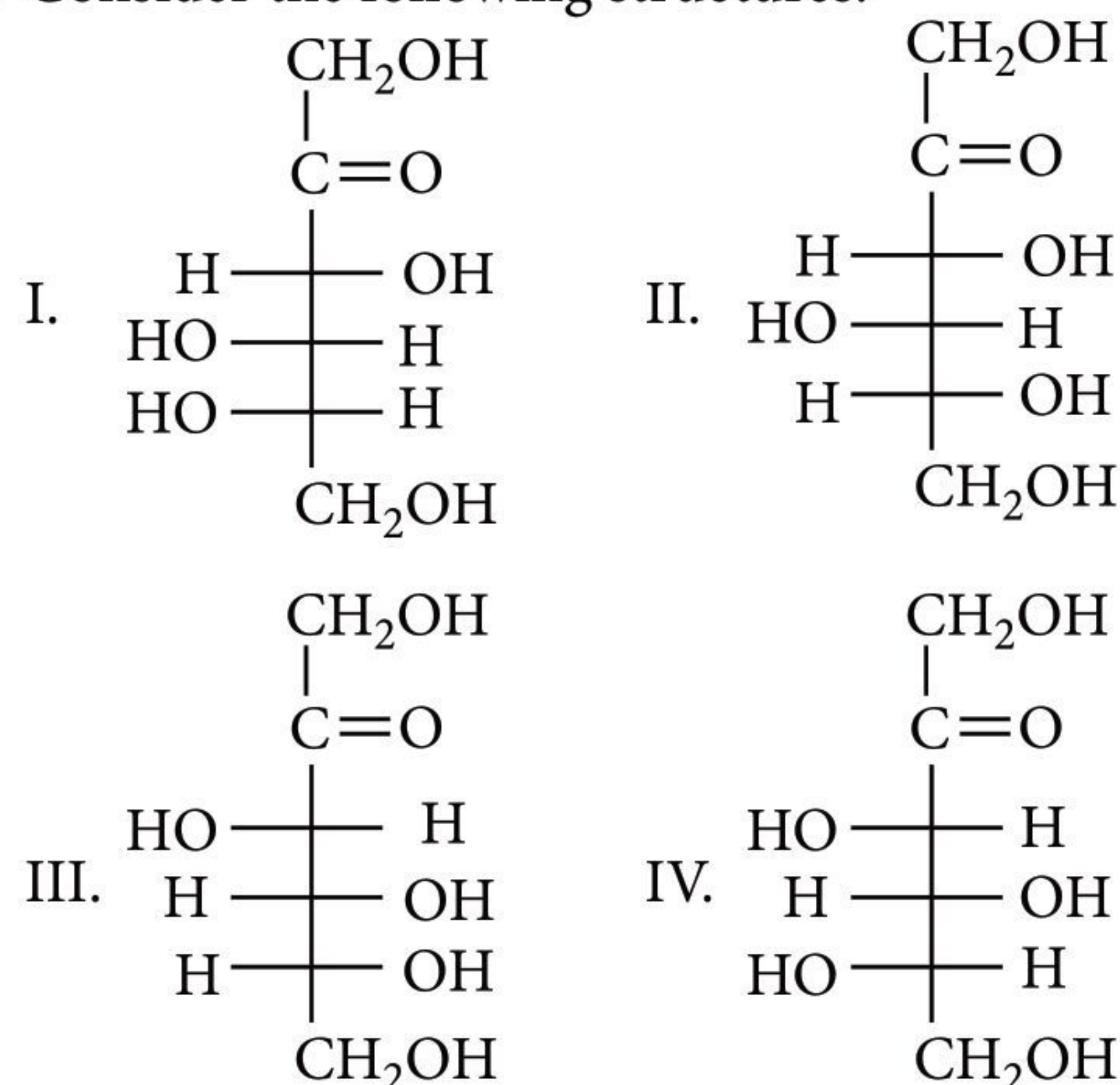
(NEET 2021)

9. The biodegradable polymer is
(a) buna-S (b) nylon-6,6
(c) nylon-2-nylon-6 (d) nylon-6

(NEET 2019)

10. In a polymer, 30% molecules have $M = 20,000$, 40% molecules have $M = 30,000$, rest of them have $M = 60,000$. Its polydispersity index is
(a) 0.83 (b) 1.45 (c) 0.98 (d) 1.20
11. Which of the following is incorrectly matched?
(a) Aspartame \rightarrow Food preservative
(b) BHT \rightarrow Antioxidant
(c) Saccharin \rightarrow Artificial sweetener
(d) Sodium benzoate \rightarrow Preservative

12. Consider the following structures.



Which of the following pairs represent *D*- and *L*-fructose respectively?

- (a) II and IV (b) I and III
(c) III and I (d) IV and II

13. Which of the following amino acids is optically inactive?

- (a) Phenyl alanine (b) Glycine
(c) Glutamic acid (d) Asparagine

14. Match the List I with List II and select the correct answer using the codes given below the list:

List I	List II
I. Iodoform	A. Anaesthetic
II. Methyl salicylate	B. Antiseptic
III. Diethyl ether	C. Insecticide
IV. Hexachlorocyclohexane	D. Detergent
	E. Pain balm

- (a) I-B, II-E, III-C, IV-D
(b) I-D, II-B, III-A, IV-C
(c) I-B, II-E, III-A, IV-C
(d) I-C, II-A, III-D, IV-B

15. Denaturation of proteins leads to loss of its biological activity by

- (a) formation of amino acids
(b) loss of primary structure
(c) loss of both primary and secondary structure
(d) loss of both secondary and tertiary structure.

16. Enzymes are essential biocatalysts. They function in

- (a) aqueous medium, temperature = 30-35°C; pH = 7
(b) organic medium
(c) aqueous medium under extreme pH conditions
(d) none of these.

17. A chemist has 4 samples of artificial sweetener A, B, C and D. To identify these samples, he performed certain experiments and noted the following observations :

- (i) A and D both form blue-violet colour with ninhydrin.
(ii) Lassaigne extract of C gives positive AgNO_3 test and negative $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ test.
(iii) Lassaigne extract of B and D gives positive sodium nitroprusside test.

Based on these observations which option is correct?

- (a) A : Alitame ; B : Saccharin ;
C : Aspartame ; D : Sucralose
(b) A : Saccharin ; B : Alitame ;
C : Sucralose ; D : Aspartame

- (c) A : Aspartame ; B : Alitame ;
C : Saccharin ; D : Sucralose

- (d) A : Aspartame ; B : Saccharin ;
C : Sucralose ; D : Alitame (JEE Main 2020)

18. Structure of (monomer unit of) natural rubber is

- (a) $\text{H}_2\text{C}=\overset{\text{CH}_3}{\underset{\text{Cl}}{\text{C}}}-\text{CH}=\text{CH}_2$
(b) $\text{H}_2\text{C}=\overset{\text{Cl}}{\underset{\text{C}_6\text{H}_5}{\text{C}}}-\text{CH}=\text{CH}_2$
(c) $\text{H}_2\text{C}=\overset{\text{C}_6\text{H}_5}{\text{C}}-\text{CH}=\text{CH}_2$
(d) $\text{CH}_2=\text{CH}_2$

19. Match Column I (name of vitamins) with Column II (deficiency disease) and select the correct option.

Column I	Column II
I. Ascorbic acid	A. Beri-beri
II. Retinol	B. Cheilosis
III. Riboflavin	C. Scurvy
IV. Thiamine	D. Night blindness

- (a) I—B; II—A; III—C; IV—D
(b) I—A; II—B; III—C; IV—D
(c) I—D; II—C; III—B; IV—A
(d) I—C; II—D; III—B; IV—A

20. Which of the following is a basic amino acid?

- (a) Serine (b) Alanine
(c) Tyrosine (d) Lysine (NEET 2020)

21. A polymer which is used as a suture, i.e., for stitching of wounds after operation is

- (a) PHBV (b) nylon-2-nylon-6
(c) dextran (d) dacron.

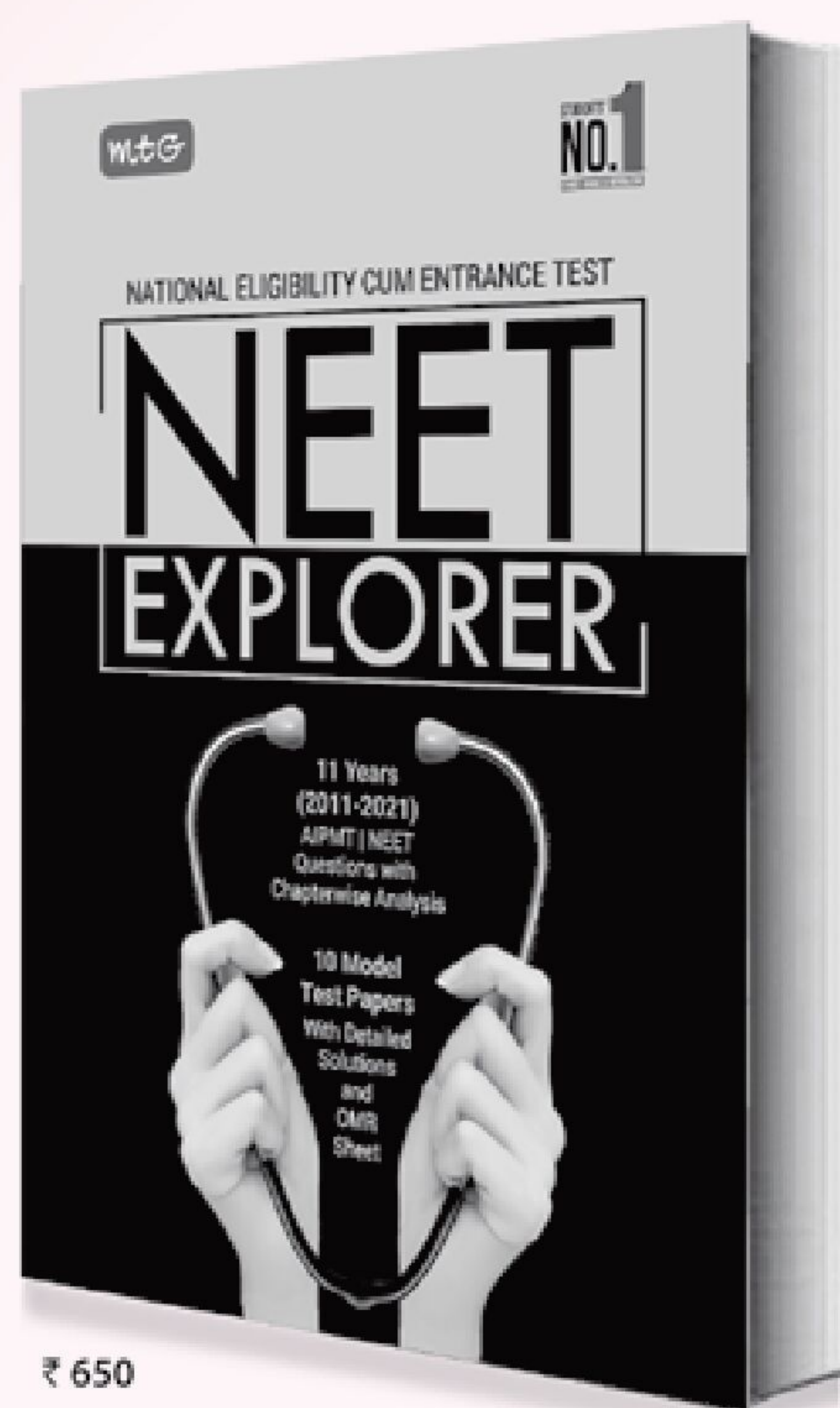
22. Polyvinyl alcohol can be prepared by

- (a) polymerisation of vinyl alcohol
(b) alkaline hydrolysis of polyvinyl acetate
(c) polymerisation of acetylene
(d) reaction of acetylene with H_2SO_4 in presence of HgSO_4 .

23. Which of the following is not true about drug receptors?

- (a) Receptor proteins are embedded in the cell membrane.
(b) The chemical known as chemical messengers are received at the binding sites of receptors.
(c) The receptors show selectivity for one chemical messenger over the other.
(d) Receptor protein is decomposed and destroyed after removal of chemical messenger.

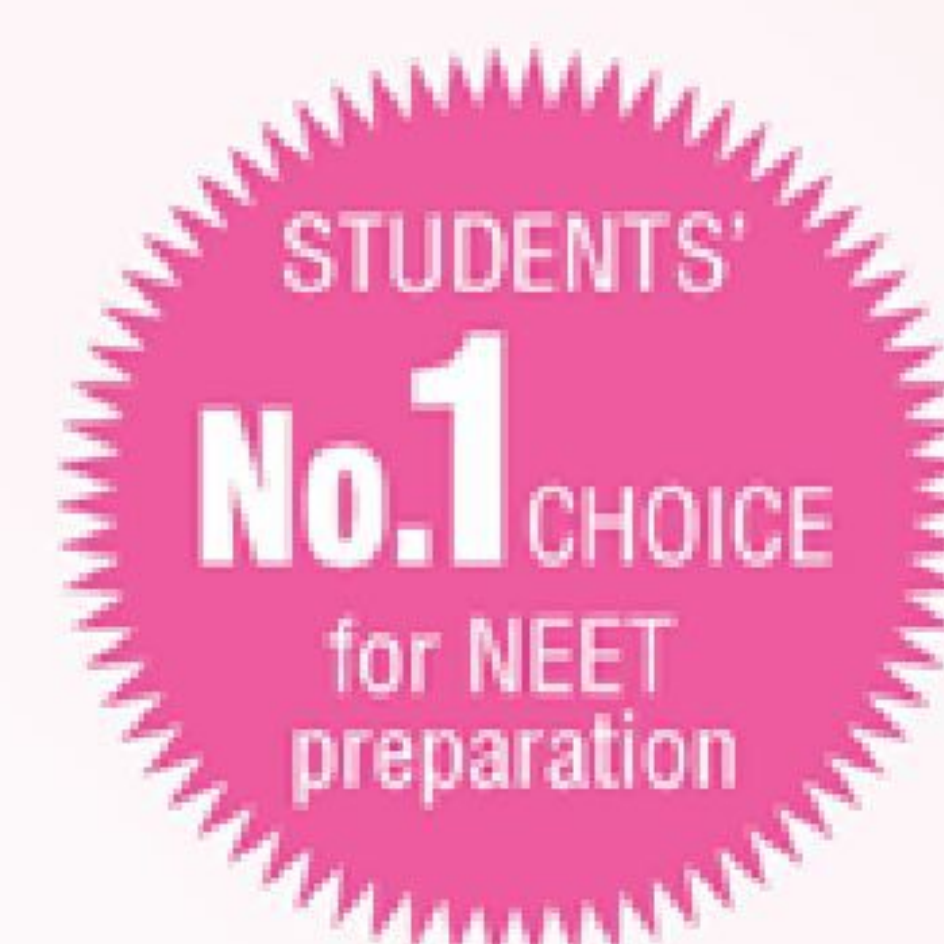
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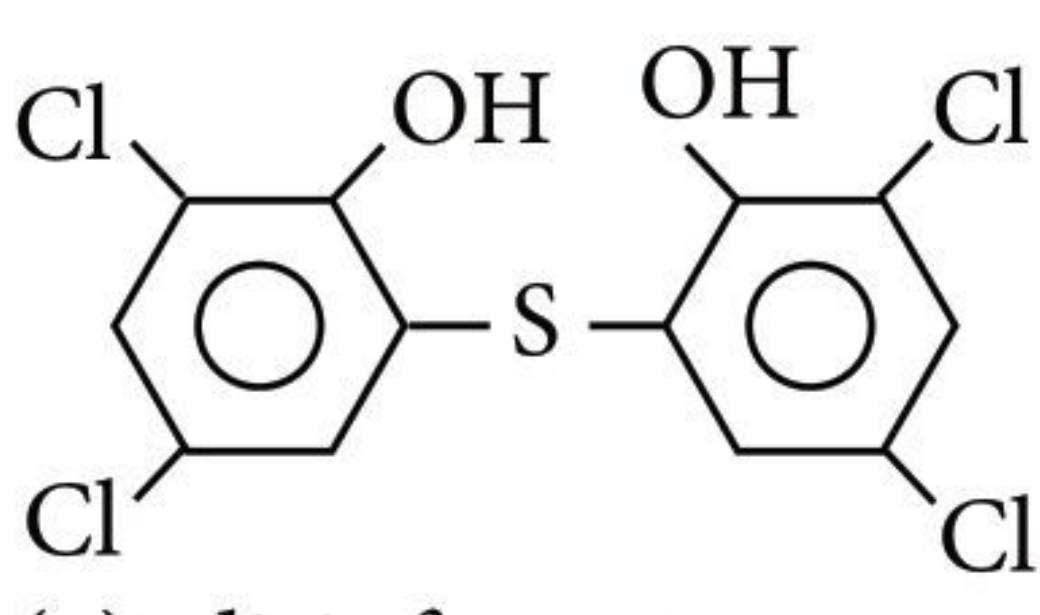
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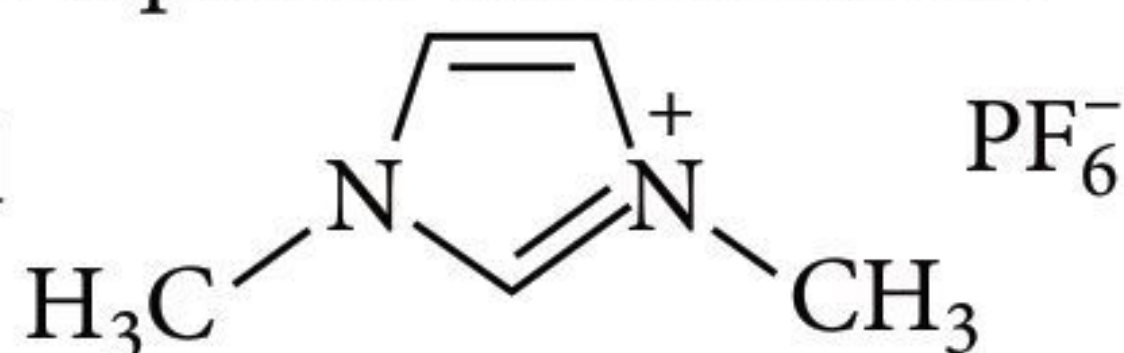
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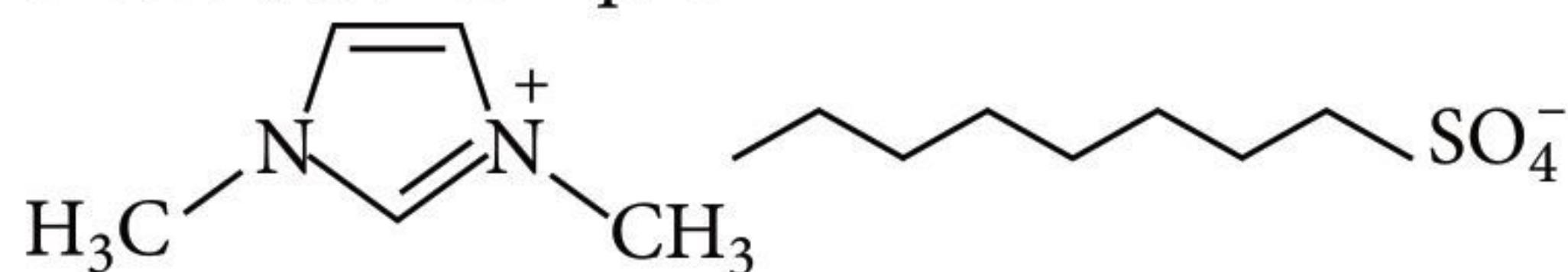
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24.  serves as a/an
 (a) disinfectant (b) antibiotic
 (c) antiseptic (d) analgesic.

25. An ionic micelle is formed on the addition of
 (a) liquid diethyl ether to aqueous NaCl solution
 (b) excess water to liquid



- (c) excess water to liquid



- (d) sodium stearate to pure toluene.

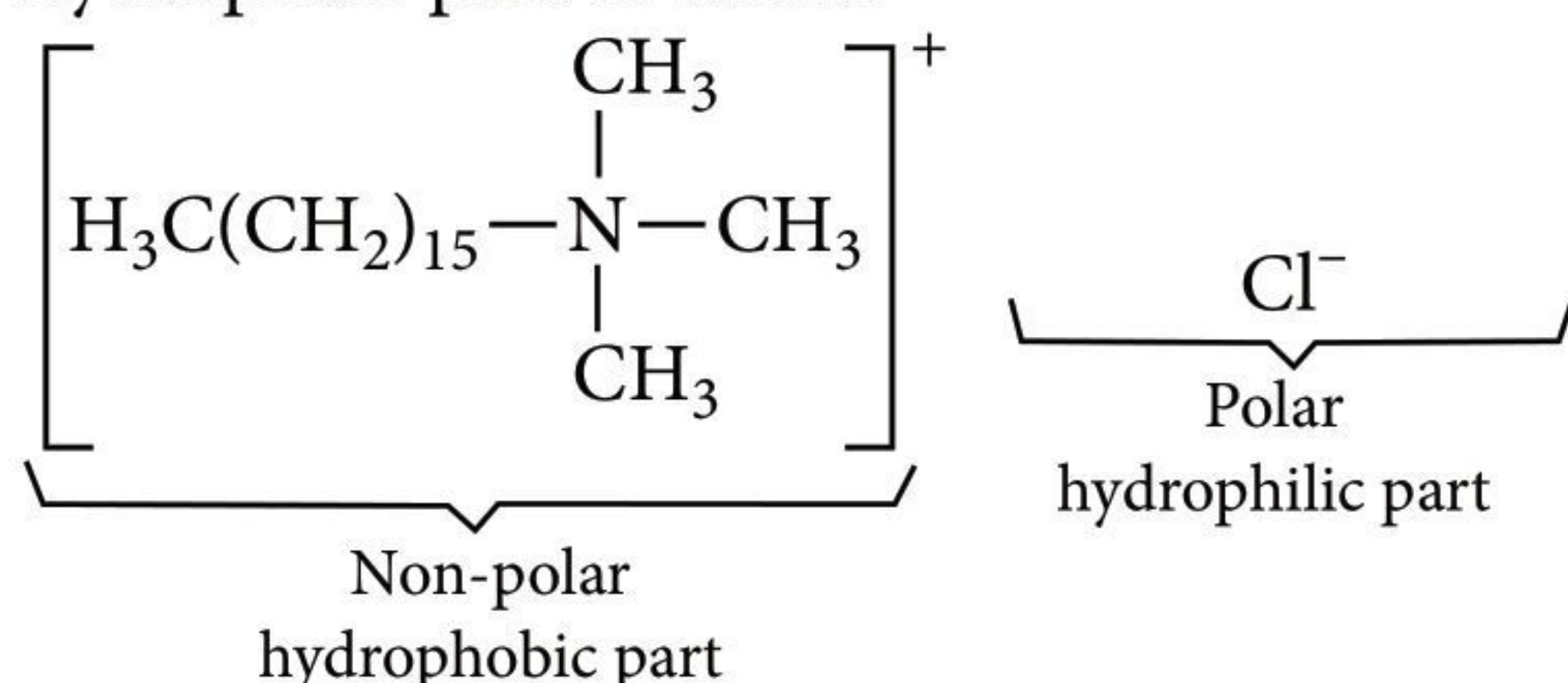
(JEE Main 2020)

NUMERICAL VALUE TYPE

26. The number of tripeptides formed by three different amino acids (having no repetition) are _____.
 27. The number of chiral carbons present in sucrose is _____. (JEE Main 2020)
 28. The mass percentage of nitrogen in histamine is _____.
 29. The number of tranquilizers among the following is _____.
 Novalgin, Equanil, Valium, Phenacetin, Ibuprofen, Meprobamate, Serotonin
 30. What percentage of sulphur is used in the vulcanization of rubber for making battery case rubber?

SOLUTIONS

1. (d): Drugs have been classified on the basis of their chemical structures, pharmacological effects, molecular targets and their action.
 2. (d): Cationic detergents are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. The cationic part possesses a long hydrocarbon chain and a positive charge on nitrogen atom. Their cleansing action is due to hydrophilic part of anion.



3. (d)

4. (b)

5. (c): Starch + I₂ → blue coloured complex

6. (b): Secondary structure of proteins is mainly of two types.

(i) α-helix: This structure is formed when the chain of α-amino acids coils as a right handed screw (called α-helix) because of the formation of hydrogen bonds between amide groups of the same peptide chain.

(ii) β-pleated sheet: In this structure the chains are held together by a very large number of hydrogen bonds between >C=O and NH of different chains.

7. (a)

8. (b): Pernicious anemia is a disease in which body does not have enough red blood cells (RBC) due to lack of vitamin B₁₂. This vitamin is needed to make red blood cells.

9. (c): Nylon-2-nylon-6 is an alternating copolymer of glycine (H₂N—CH₂—COOH) and caproic acid [H₂N(CH₂)₅COOH] and is biodegradable.

$$10. (d): PDI = \frac{\bar{M}_w}{\bar{M}_n}; \bar{M}_n = \frac{M_1N_1 + M_2N_2 + M_3N_3}{N_1 + N_2 + N_3}$$

$$= \frac{20000 \times 30 + 30000 \times 40 + 60000 \times 30}{30 + 40 + 30}$$

$$= \frac{6 \times 10^5 + 12 \times 10^5 + 18 \times 10^5}{100} = 36 \times 10^3$$

$$\bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{M_1N_1 + M_2N_2 + M_3N_3}$$

$$= \frac{30(20000)^2 + 40(30000)^2 + 30(60000)^2}{30 \times 20,000 + 40(30000) + 30 \times 60000}$$

$$= \frac{1.2 \times 10^{10} + 3.6 \times 10^{10} + 10.8 \times 10^{10}}{36 \times 10^5} = \frac{15.6 \times 10^{10}}{36 \times 10^5}$$

$$PDI = \frac{15.6 \times 10^{10} / 36 \times 10^5}{36 \times 10^3} = \frac{15.6 \times 10^{10}}{36 \times 36 \times 10^8} = 1.20$$

11. (a): Aspartame is an artificial sweetener.

12. (c)

13. (b): Glycine (H₂N—CH₂—COOH) is the only amino acid that is not having any chiral carbon, hence it is achiral and optically inactive.

14. (c)

15. (d): Denaturation results in loss of both secondary and tertiary structures while primary structure remains intact.

16. (a): Enzymes function most efficiently in aqueous medium at a temperature 30-35°C and pH = 7.

17. (d): (i) Aspartame (*A*) and alitame (*D*) give positive test with ninhydrin because both have free carboxylic and amine groups.

(ii) Sucralose (C) form precipitate with AgNO_3 in the Lassaigne extract of the sugar because it has chlorine atoms.

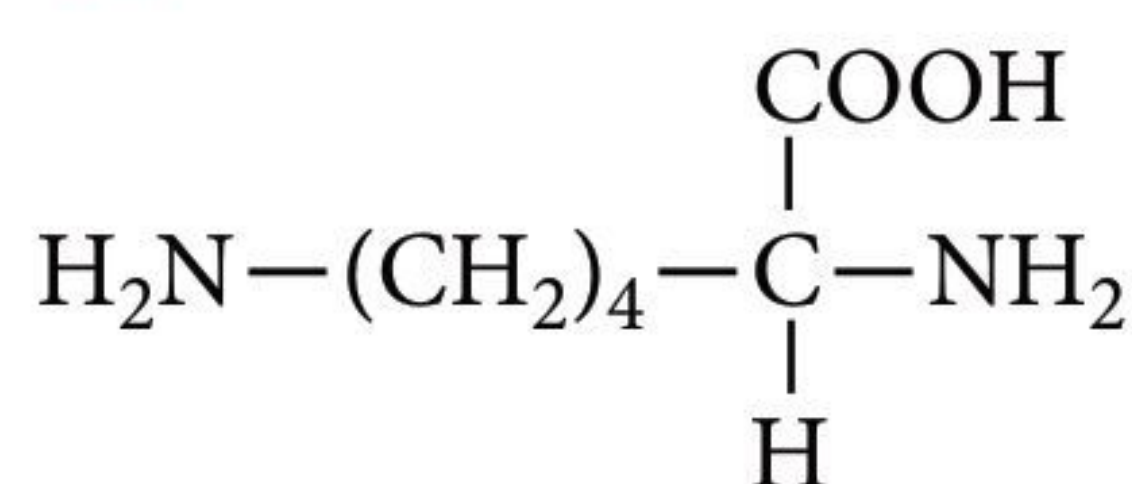
(iii) Saccharin (*B*) and alitame (*D*) give positive test with sodium nitroprusside because both have sulphur atoms.

18. (a)

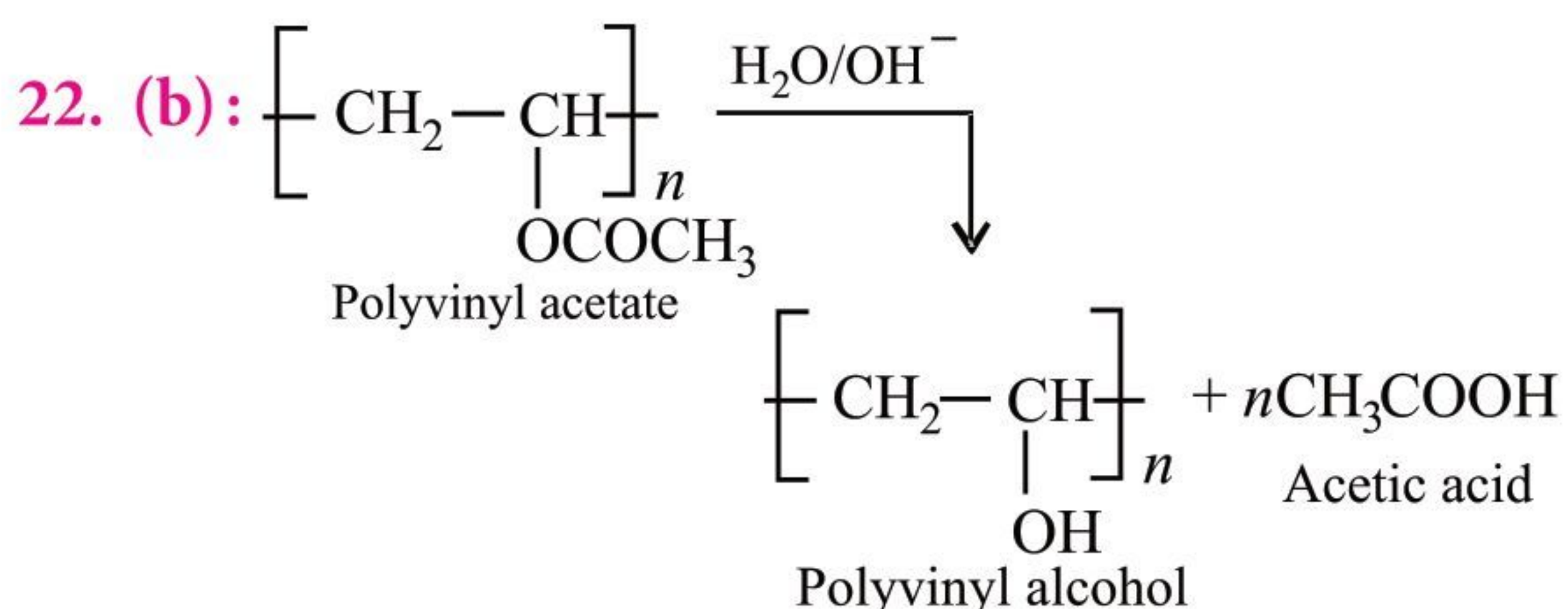
19. (d):Vitamin	Deficiency disease
------------------------	---------------------------

Ascorbic acid (Vitamin C)	Scurvy
Retinol (Vitamin A)	Night blindness
Riboflavin (Vitamin B ₂)	Cheilosis
Thiamine (Vitamin B ₁)	Beri-beri

20. (d): Lysine is a basic amino acid.



21. (c) : Dextran is used for post operative stitches.

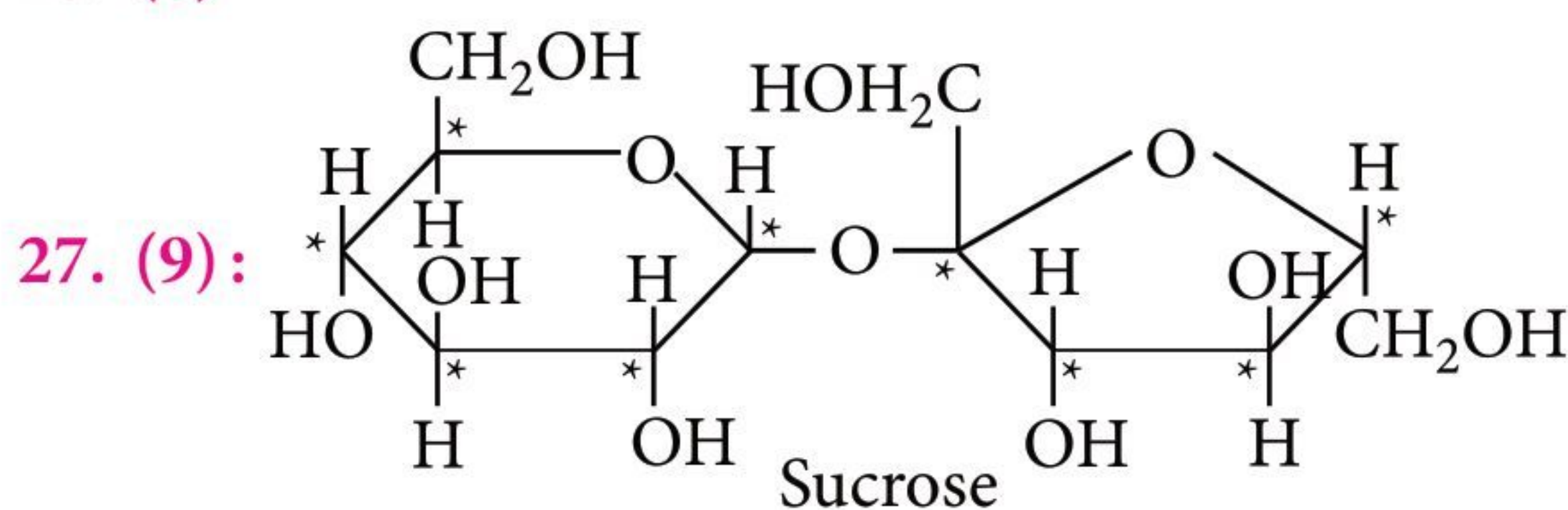


23. (d): Receptor regains its structure and shape after removal of chemical messenger.

24. (c) : The given structure is of bithional and it is used as an antiseptic.

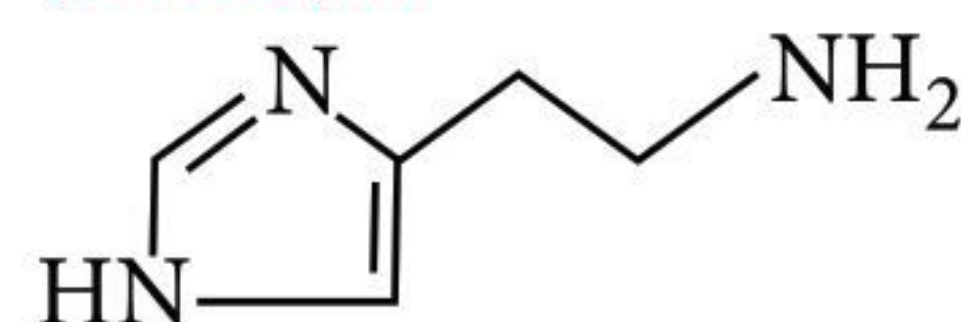
25. (c) : Ionic micelles are formed by addition of water to soap.

26. (6)



* represents chiral carbon atom.

28. (37.83) : Structure of histamine :



Molecular formula : $\text{C}_5\text{H}_9\text{N}_3$

Molecular mass of histamine = 111

Mass percentage of nitrogen

$$= \frac{\text{Mass of nitrogen}}{\text{Molecular mass of histamine}} \times 100$$

$$= \frac{42}{111} \times 100 = 37.83\%$$

29. (4): Equanil, valium, meprobamate, serotonin are tranquilizers.

30. (30)

For the
SCIENTIST in
YOU

Heavy oil-eating microbe grown in the lab for the first time!!

A microorganism capable of converting oil into methane has been cultivated by researchers in Germany, China and Spain. The single-celled organism, an archaeon called *Candidatus methanoliparum*, breaks down oil into methane and carbon dioxide. Unlike other archaea that live on short-chain hydrocarbons like ethane or butane, *methanoliparum* prefers heavy oil and its long-chain compounds.

'Methanoliparia is a kind of hybrid creature that combines the properties of an oil degrader with those of a methanogen, i.e. a methane producer,' explained study leader, from a marine microbiology in a press release.

The international research team was able to grow these microorganisms in the lab for the first time. It turns out that methanoliparium consumes long-chain alkanes as well as cyclohexanes and benzenes with alkyl substituents longer than 13 carbon atoms while shunning ethane, octane and aromatics with shorter alkyl chains.

Methanoliparium's genetic make-up means that it carries the blueprints for enzymes that can activate and decompose various hydrocarbons as well as 'the complete gear kit of a methane producer'. Nevertheless, it activates all hydrocarbons with just one enzyme. Lab-grown methanoliparia could be used for microbial-enhanced energy recovery from depleted oil reservoirs, the researchers state.



CBSE

warm-up!

Term-II

CLASS-XII

Series-2

Chemical Kinetics | Surface Chemistry |
Coordination Compounds | Amines

Time Allowed : 2 hours
Maximum Marks : 35

General Instructions : Read the following instructions carefully.

1. There are 12 questions in this question paper with internal choice.
2. SECTION A - Q. No. 1 to 3 are very short answer questions carrying 2 marks each.
3. SECTION B - Q. No. 4 to 11 are short answer questions carrying 3 marks each.
4. SECTION C - Q. No. 12 is case based question carrying 5 marks.
5. All questions are compulsory.
6. Use of log tables and calculators is not allowed.

SECTION - A

1. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the concentration of the reactant to 1/10th of its initial value?
2. (a) What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when
(i) $\Delta_o > P$ (ii) $\Delta_o < P$
(b) Write two limitations of crystal field theory.
3. How does adsorption of a gas on a solid surface vary with temperature? Illustrate with the help of appropriate graphs.

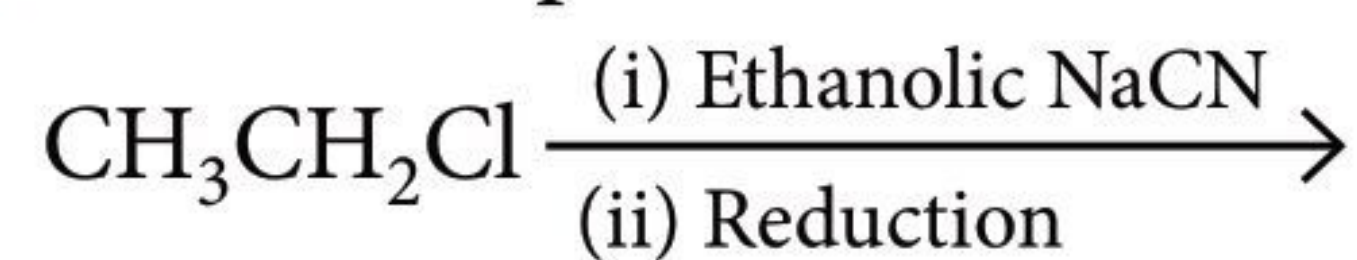
SECTION - B

4. (i) Dilute equimolar solutions of each of the following compounds were prepared. Arrange these compounds in increasing order of molar conductivity of their solutions.
(a) $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (b) $\text{K}[\text{Co}(\text{EDTA})]$

- (c) $[\text{Co}(\text{py})_3(\text{CN})_3]$ (d) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
(e) $[\text{Pt}(\text{NH}_3)_6]\text{Br}_4$

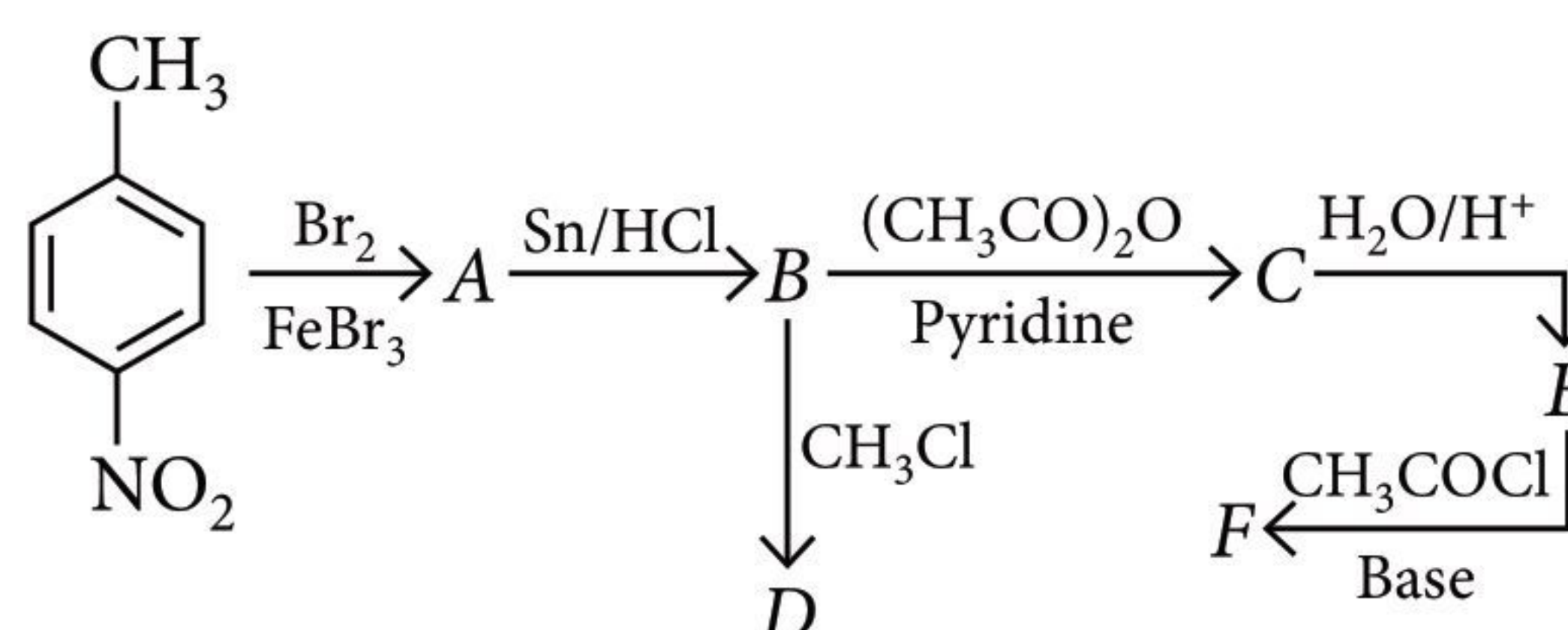
(ii) For the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. (At. number Fe = 26)

5. (i) Account for the following :
(a) Like ammonia, amines are good nucleophiles.
(b) Aryl amines are weaker bases than alkyl amines.
(ii) Predict the product of the following reaction :



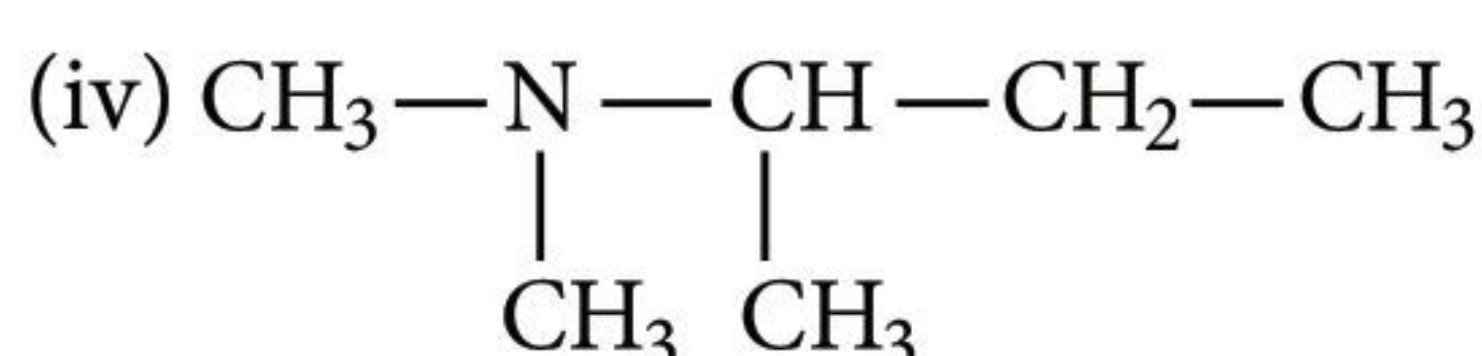
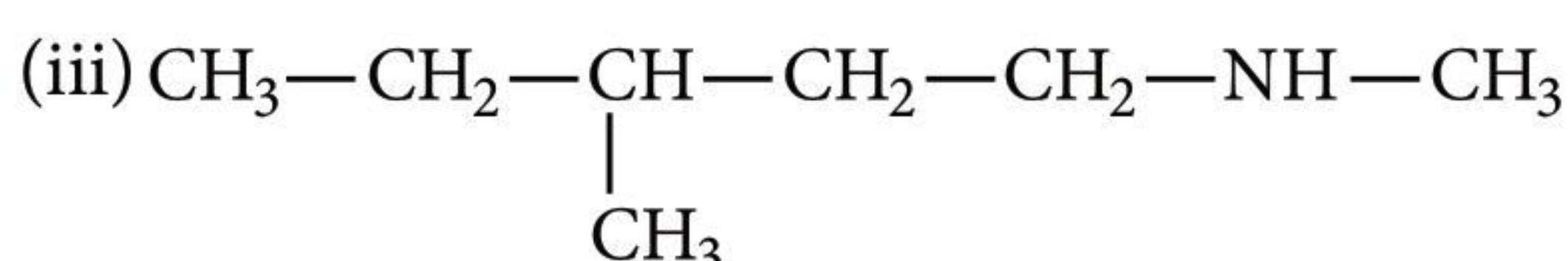
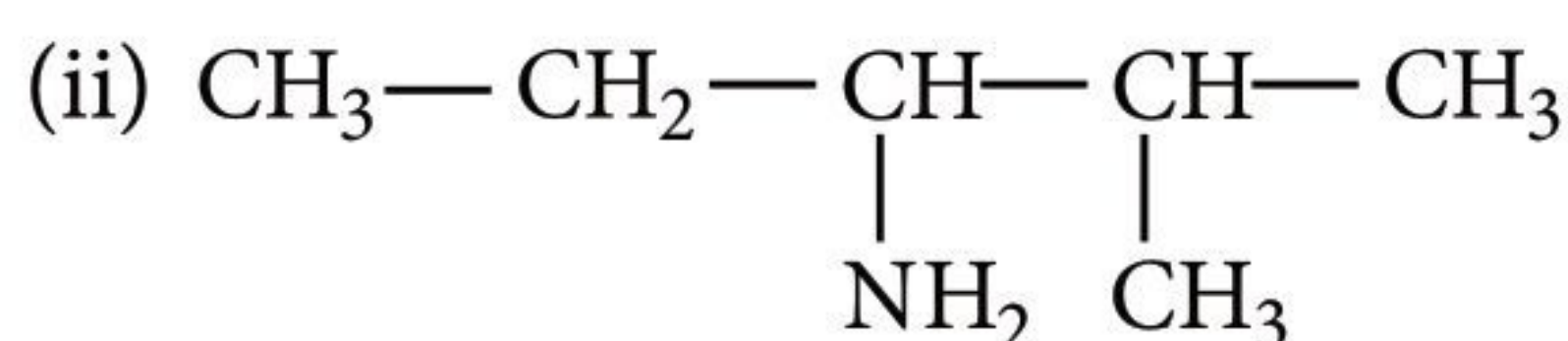
OR

Complete the following sequence of reactions and identify the products, A, B, C, D, E and F.



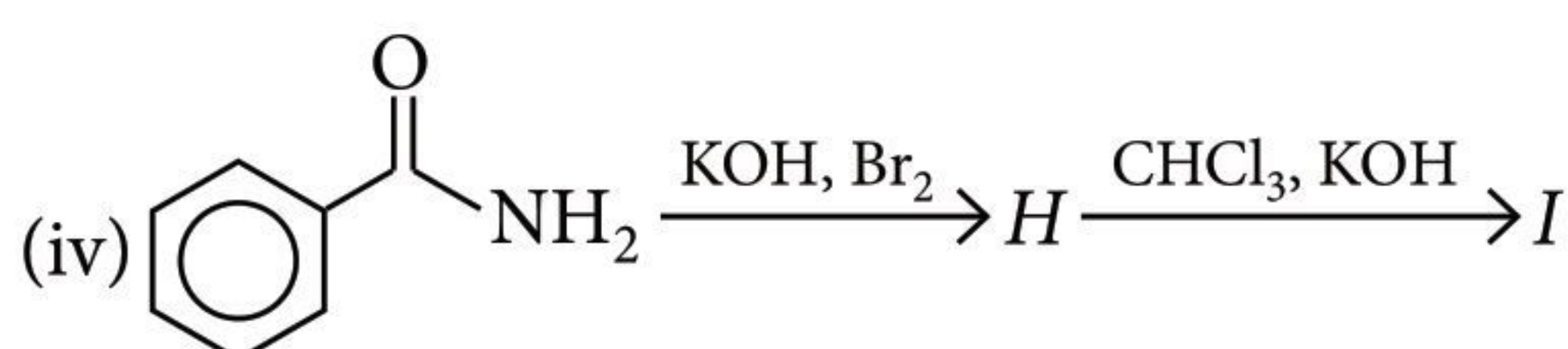
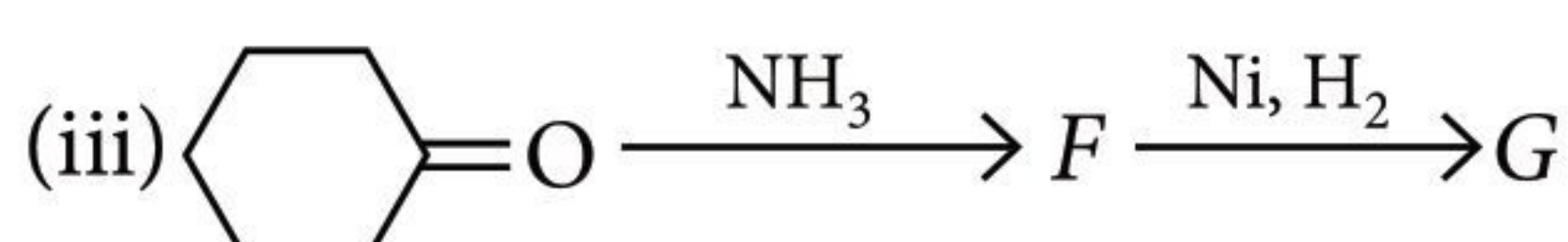
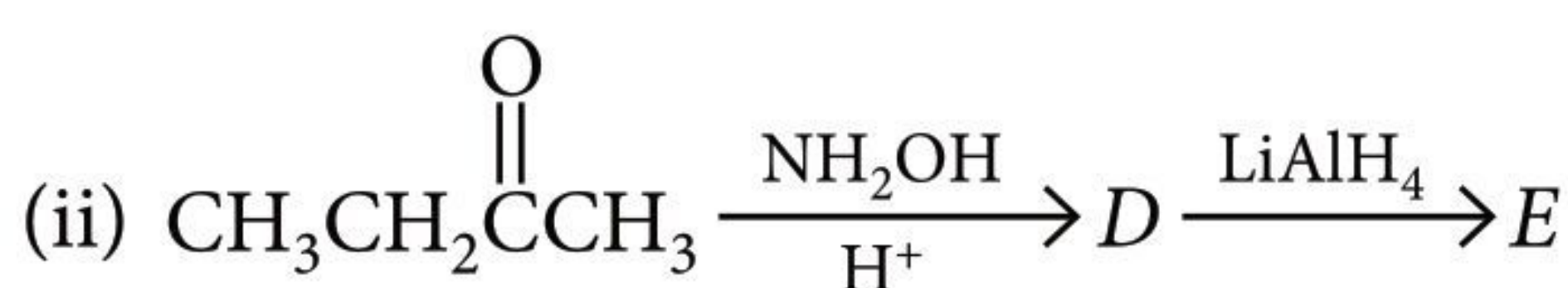
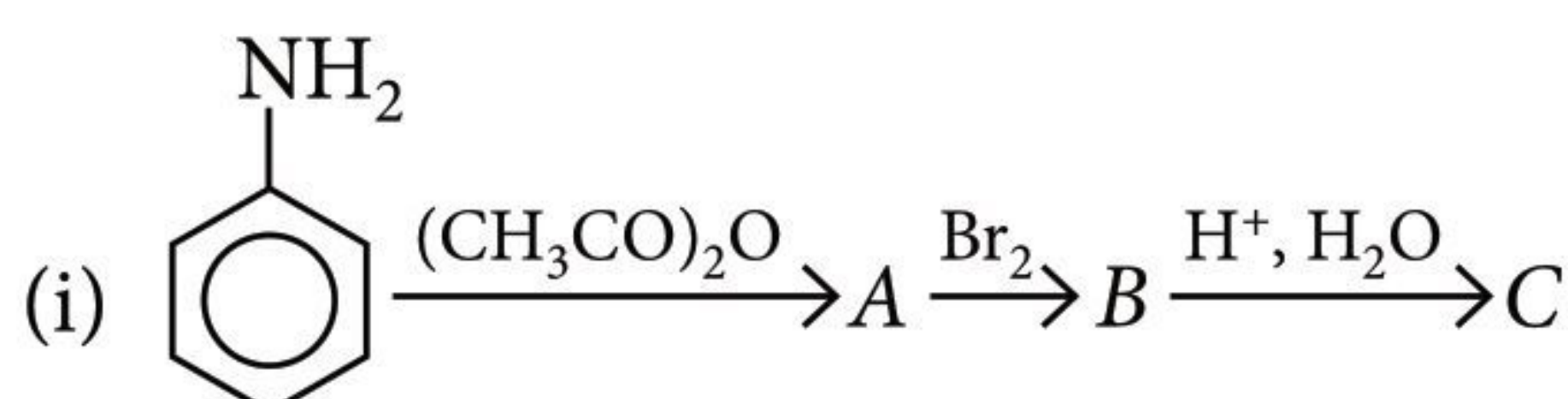
6. (a) Carry out the conversion of bromomethane to ethanol.

(b) Write the IUPAC name for the following:



OR

Complete the following reaction sequence and identify the products A, B, C, D, E, F, G, H and I.



7. (i) If half-lives of a first order and zero order reactions are same, then calculate the ratio of the initial rates of the first order reaction to that of zero order reaction.

(ii) For the first order reaction, show that the time required for 99% completion is twice the time required for 90% completion.

OR

(i) In the reaction, $\text{A} + 2\text{B} \longrightarrow \text{C} + 2\text{D}$, the rate of change of [A] is $2.8 \times 10^{-2} \text{ M s}^{-1}$. Calculate the corresponding rate of change of [D].

(ii) The gaseous reaction, $\text{A}_{(g)} \longrightarrow 2\text{B}_{(g)} + \text{C}_{(g)}$ is found to be first order. If the reaction is started with $p_A = 90 \text{ mm Hg}$, the total pressure after

10 minutes is found to be 180 mm Hg. Calculate the rate constant of the reaction. [$\log 2 = 0.301$]

8. Account for following :

(a) Define micelles.

(b) Define multimolecular colloids with examples.

(c) What are the two processes involved in Bredig's arc method?

9. Write the name, the structure and the magnetic behaviour of each one of the following complexes :

(i) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$

(ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

(iii) $\text{Ni}(\text{CO})_4$

(At. nos. Co = 27, Ni = 28, Pt = 78)

10. Nitrogen pentoxide decomposes according to the equation : $2\text{N}_2\text{O}_{5(g)} \longrightarrow 4\text{NO}_{2(g)} + \text{O}_{2(g)}$

This first order reaction was allowed to proceed at 40°C and the data given below were collected :

$[\text{N}_2\text{O}_5] \text{ (M)}$	Time (min)
0.400	0.00
0.289	20.00
0.209	40.00
0.151	60.00
0.109	80.00

(i) Calculate the rate constant for the reaction. Include units with your answer.

[Given : $\log 4 = 0.6021$, $\log 2.89 = 0.469$].

(ii) Calculate the initial rate of reaction.

(iii) After how many minutes will $[\text{N}_2\text{O}_5]$ be equal to 0.350 M?

11. For Freundlich adsorption isotherm, a plot of $\log (x/m)$ (y-axis) and $\log p$ (x-axis) gives a straight line. The intercept and slope for the line is 0.4771 and 2, respectively. What is the mass of gas, absorbed per gram of adsorbent if the initial pressure is 0.04 atm. ($\log 3 = 0.4771$)



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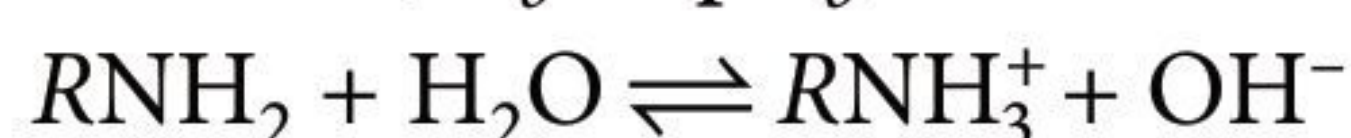
OR

- Define adsorption isotherms.
- Explain the phenomenon of adsorption in the production of vacuum.
- Write one difference between solution and colloid.

SECTION - C

12. Read the passage given below and answer the questions that follow:

Amines are basic in nature. The basic strength of amines can be expressed by their dissociation constant, K_b or pK_b .



$$K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \quad \text{and} \quad pK_b = -\log K_b$$

Greater the K_b value or smaller the pK_b value, more is the basic strength of amine. Aryl amines such as aniline are less basic than aliphatic amines due to the involvement of lone pair of electrons on N-atom with the resonance in benzene. Electron-donating groups such as $-\text{CH}_3$, $-\text{OCH}_3$, etc. increase the basicity while electron-withdrawing substitutes such as $-\text{NO}_2$, $-\text{CN}$, halogens, etc. decrease the basicity of amines. The effect of these substituents is more at *p*-than at *m*-positions.

- Which has the lowest pK_b value between aniline and *N,N*-dimethylaniline? Explain.
- Arrange the following in the decreasing order of basicity: Aniline, *o*-toluidine, *m*-toluidine
- Why are amines less acidic than alcohols of comparable molecular masses?
- Arrange the following compounds in increasing order of solubility in water:
 $\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

OR

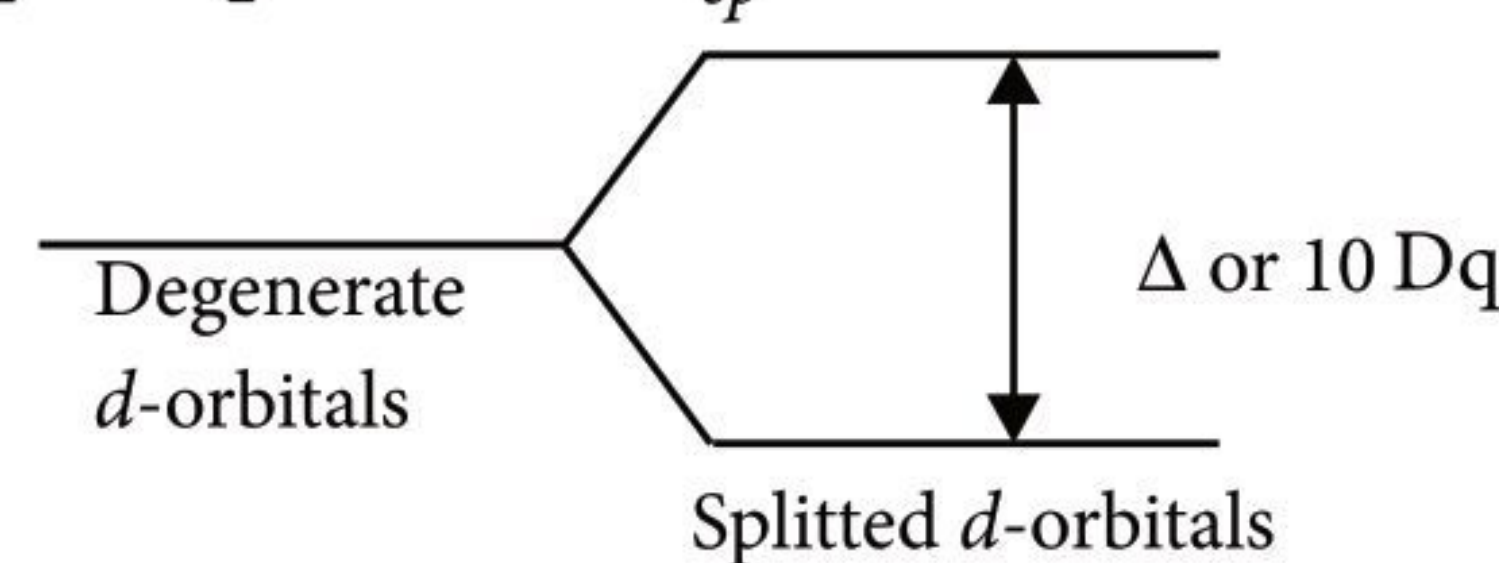
Aniline is a weaker base than cyclohexylamine. Explain.

SOLUTIONS

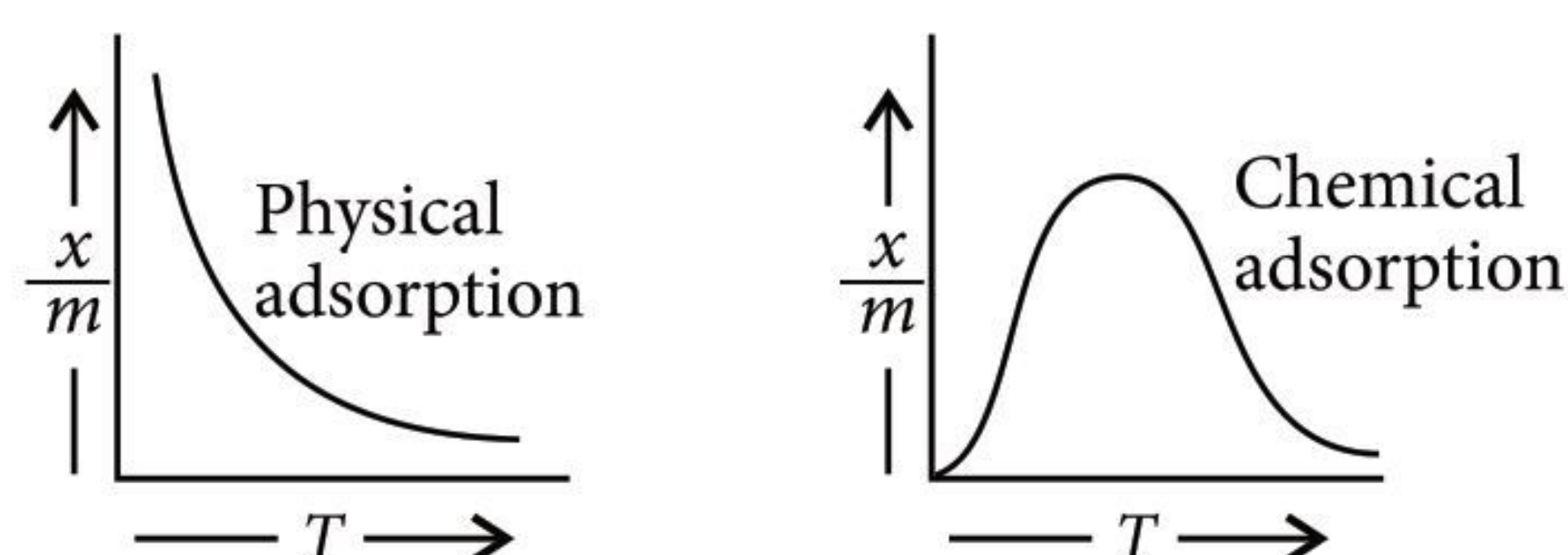
1. For a first order reaction, $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$
 $k = 60 \text{ s}^{-1}$, $[A] = [A]_0/10$
 Now, $t = \frac{2.303}{60} \log \frac{[A]_0}{[A]_0/10} = \frac{2.303}{60} \log 10$
 $= 0.038 \text{ s}$ or $3.8 \times 10^{-2} \text{ s}$

2. (a) The difference of energy between two splitted levels of *d*-orbitals is called crystal field splitting energy. It is denoted by Δ or $10 Dq$.

For octahedral, it is denoted as Δ_o , for tetrahedral it is Δ_t and for square planar as Δ_{sp} .



- When $\Delta_o > P$, $t_{2g}^4 e_g^0$
 - When $\Delta_o < P$, $t_{2g}^3 e_g^1$
- (b) (i) It assumes ligands to be point charges.
 (ii) It does not take into account the covalent character of bonding between the ligand and the central atom.
3. Physical adsorption of a gas on a solid decreases with increase in temperature while chemical adsorption first increases and then decreases with increase in temperature.

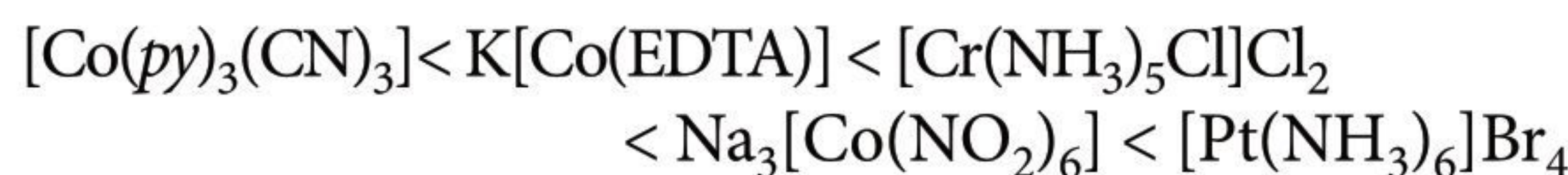


$\frac{x}{m}$ represents the extent of adsorption where x is the mass of adsorbate and m is the mass of adsorbent.

4. (i) These compounds will ionise as follows in their solutions:

- $\text{Na}_3[\text{Co}(\text{NO}_2)_6] \rightleftharpoons 3\text{Na}^+ + [\text{Co}(\text{NO}_2)_6]^{3-}$
 $= 4 \text{ ions}$
- $\text{K}[\text{Co}(\text{EDTA})] \rightleftharpoons \text{K}^+ + [\text{Co}(\text{EDTA})]^-$
 $= 2 \text{ ions}$
- $[\text{Co}(\text{py})_3(\text{CN})_3]$
 No ionisation (molecular complex)
- $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightleftharpoons [\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$
 $= 3 \text{ ions}$
- $[\text{Pt}(\text{NH}_3)_6]\text{Br}_4 \rightleftharpoons [\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Br}^-$
 $= 5 \text{ ions}$

As molar conductivity is proportional to the number of ions produced in the solution, therefore, the order is as follows:



- (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$: Fe atom ($Z = 26$)

Ground state: $1s^2 2s^2 2p^6 3s^2 3p^4 4s^2$

Fe^{3+} ion: $1s^2 2s^2 2p^6 3s^2 3p^4$

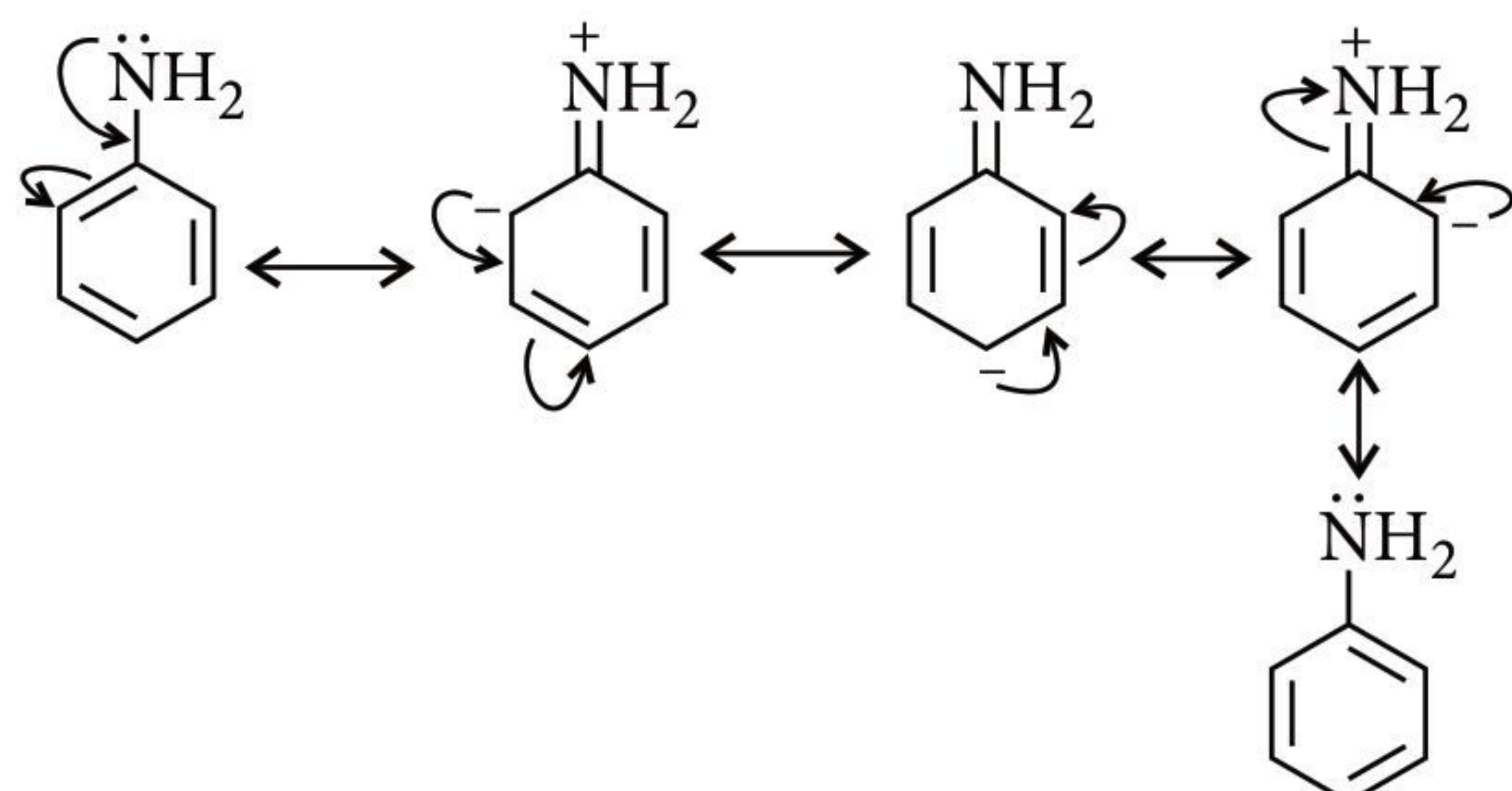
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^4 4s^2 4p^6 4d^5$

sp^3d^2 hybridisation
 six pairs of electrons
 from six H_2O ligands
 (weak field ligand)

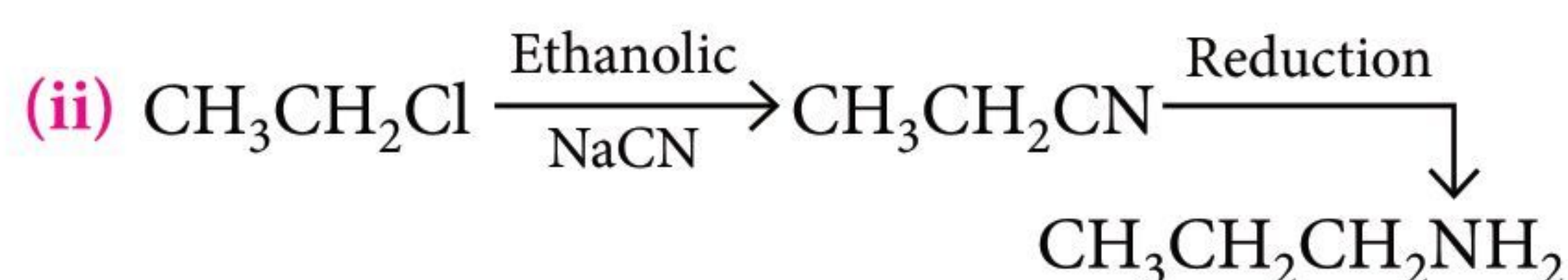
The complex ion has outer orbital octahedral geometry (high spin) and is paramagnetic due to the presence of five unpaired electrons.

5. (i) (a) Amines like ammonia are good nucleophiles. This is because alkyl group in an amine shows electron releasing effect. This increases the electron density on 'N' of amino group and hence, makes the amines very good nucleophiles.

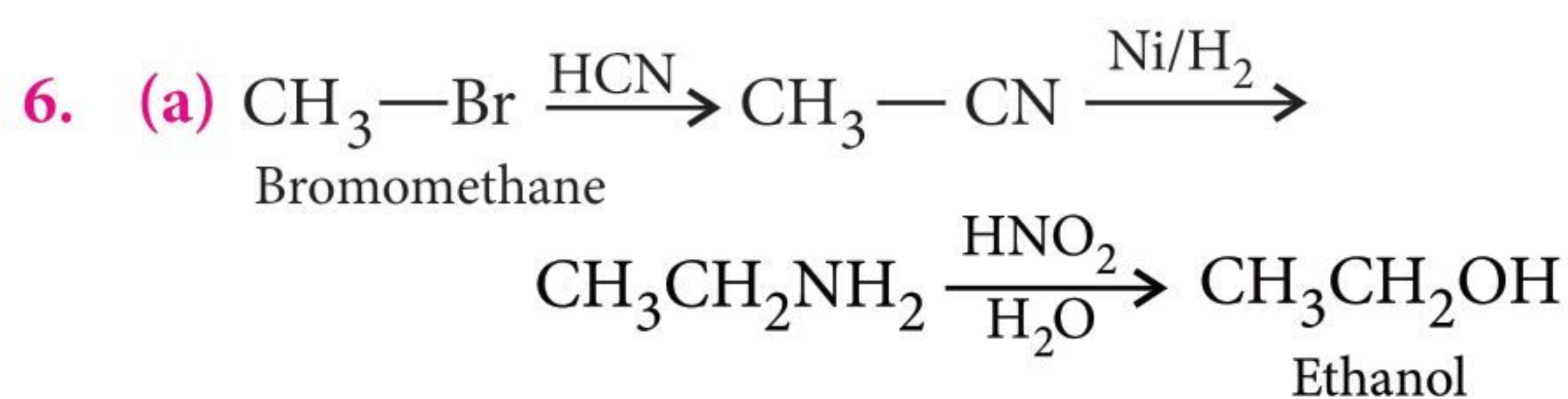
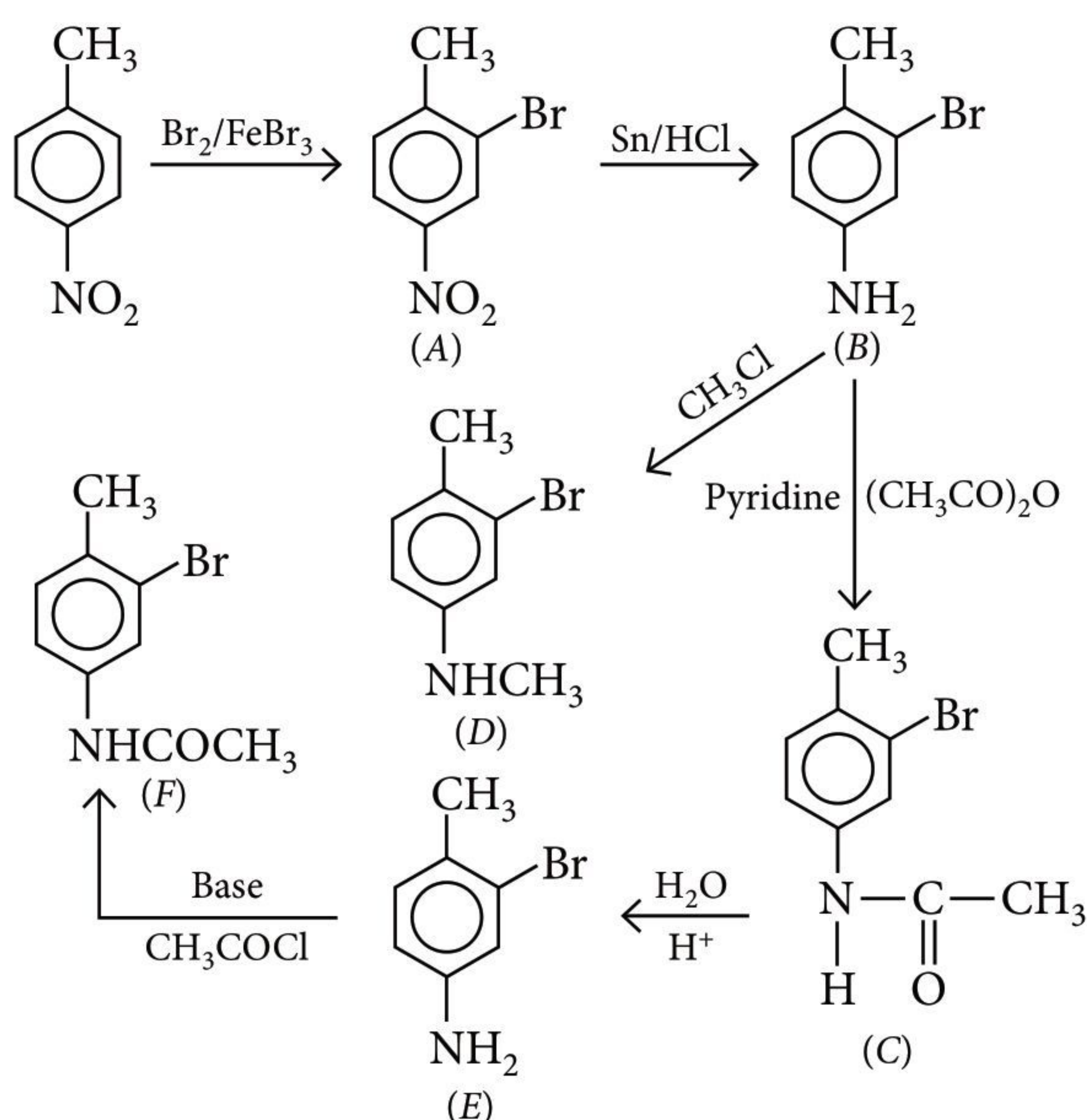
(b) Due to resonance in aryl amines, the lone pair of electrons on nitrogen gets delocalised over the benzene ring and becomes less available for protonation.



In alkyl amine, alkyl group releases electrons and increases electron density on nitrogen, making it stronger base.

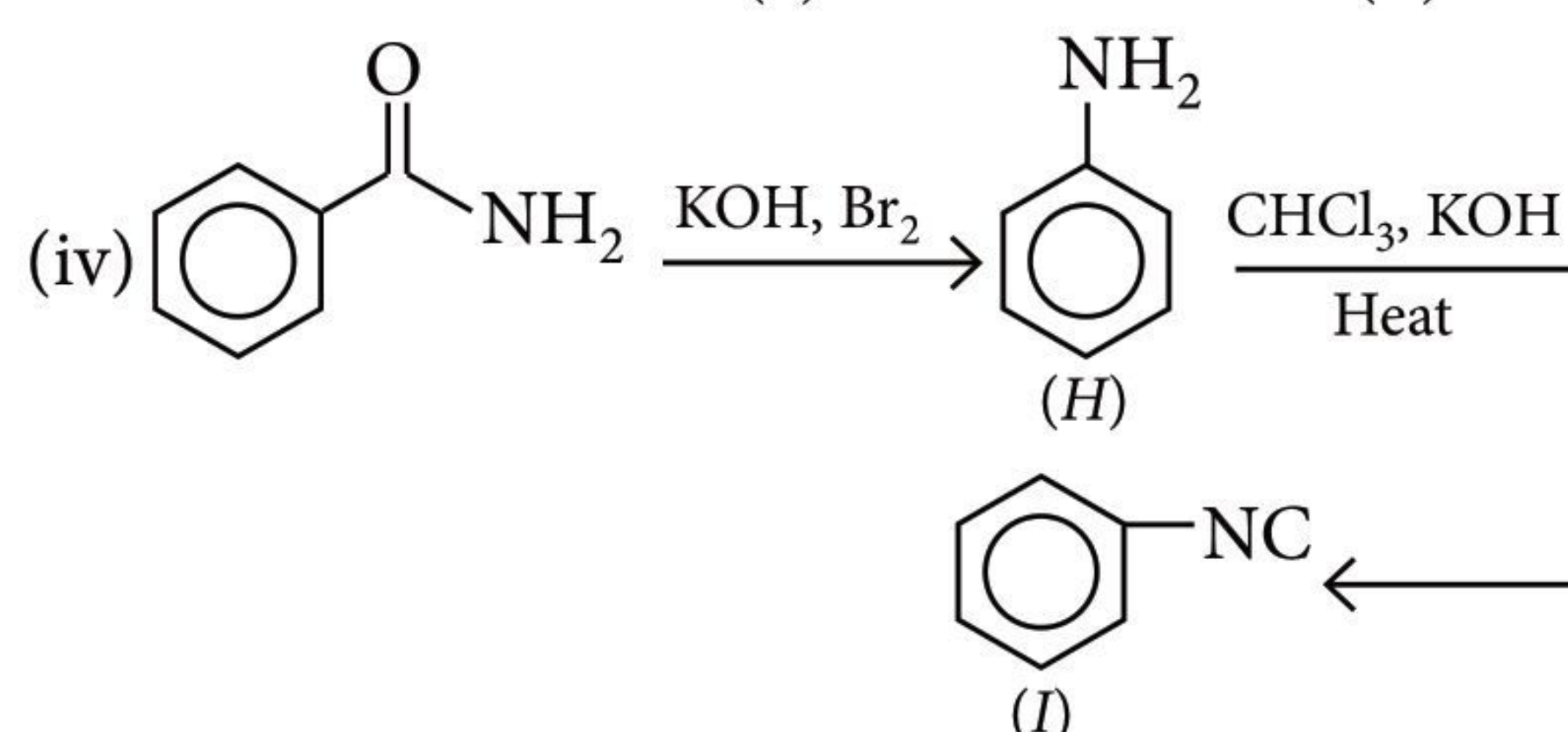
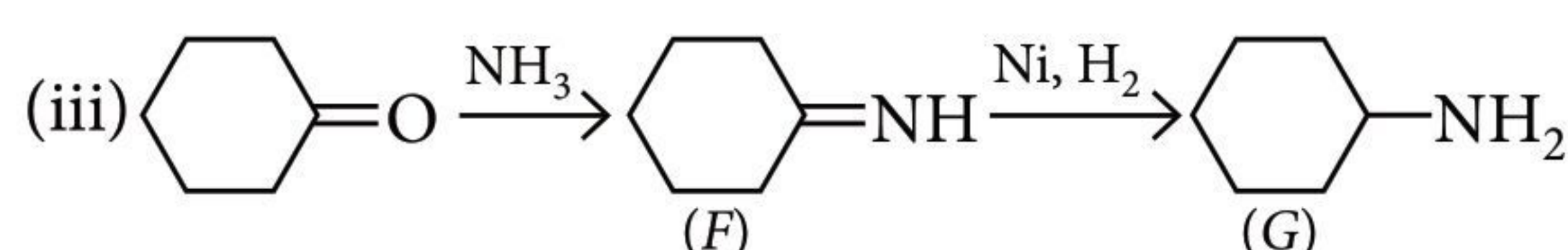
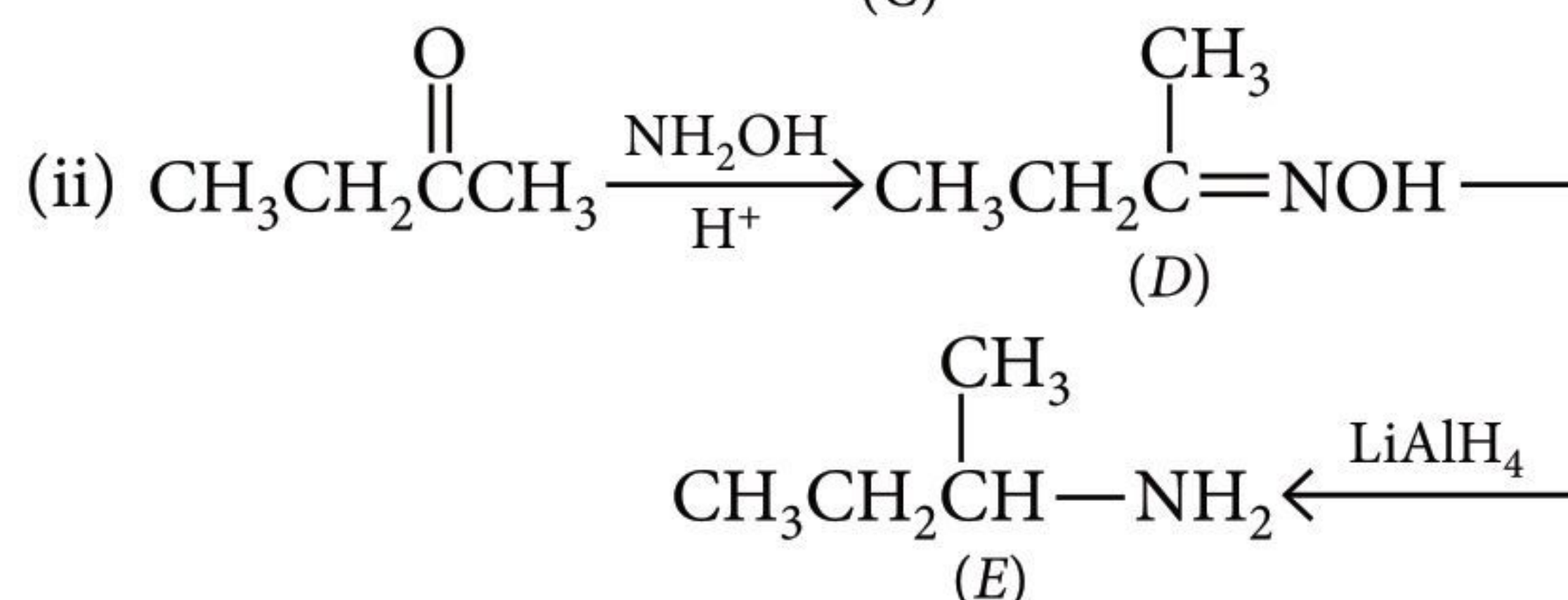
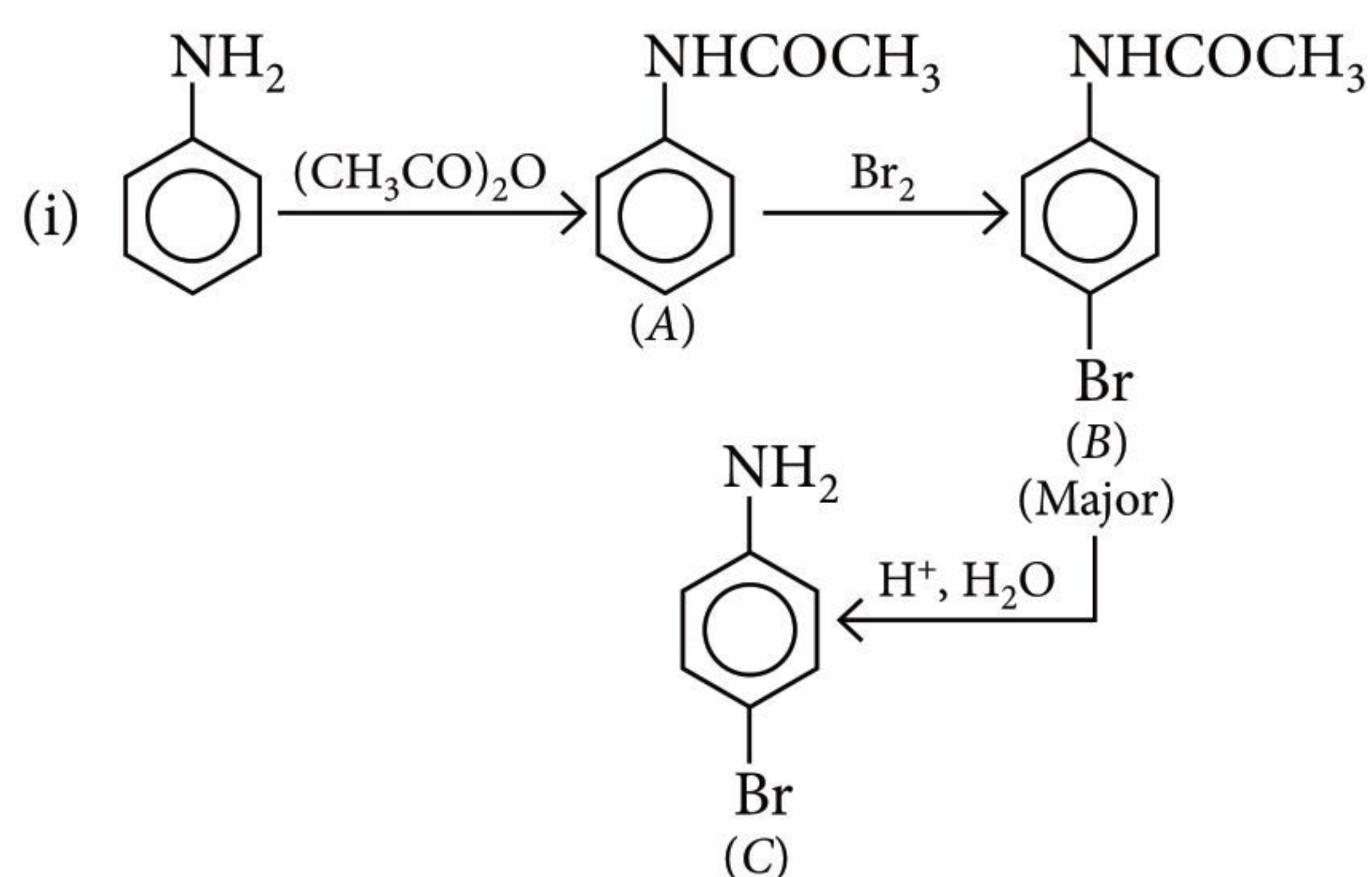


OR



- (b) (i) 1-Phenylethanamine
 (ii) 2-Methylpentan-3-amine
 or 2-Methyl-3-pentanamine
 (iii) 3-Methyl-1-(N-methylamino)pentane
 or 3-Methyl-N-methylpentanamine
 (iv) 2-(N,N-Dimethylamino)butane

OR



MONTHLY TEST DRIVE CLASS XI ANSWER KEY

- | | | | | |
|--------------|-----------|-----------|---------|--------------|
| 1. (a) | 2. (d) | 3. (a) | 4. (d) | 5. (c) |
| 6. (a) | 7. (a) | 8. (a) | 9. (b) | 10. (d) |
| 11. (c) | 12. (a) | 13. (b) | 14. (c) | 15. (b) |
| 16. (b) | 17. (c) | 18. (b) | 19. (c) | 20. (a,d) |
| 21. (a, b,d) | 22. (b,d) | 23. (a,b) | 24. (3) | 25. (428.57) |
| 26. (8.029) | 27. (c) | 28. (b) | 29. (b) | 30. (b) |

7. (i) For first order reaction, $t_{1/2} = \frac{0.693}{k}$

For zero order reaction, $t_{1/2} = \frac{[A]_0}{2k'}$

Initial rate for first order, $r_1 = k[A]_0$

Initial rate for zero order, $r_0 = k'$

$$\therefore \frac{r_1}{r_0} = \frac{k[A]_0}{k'}; \text{As } \frac{0.693}{k} = \frac{[A]_0}{2k'}$$

$$\therefore \frac{k[A]_0}{k'} = 2 \times 0.693 \text{ or } \frac{r_1}{r_0} = 2 \times 0.693 = 1.386$$

$$(ii) kt_{99\%} = 2.303 \log \frac{a}{\frac{1}{100}a}$$

$$\Rightarrow kt_{99\%} = 2.303 \log 10^2 \quad \dots(i)$$

$$kt_{90\%} = 2.303 \log \frac{a}{\frac{10}{100}a}$$

$$\Rightarrow kt_{90\%} = 2.303 \log 10 \quad \dots(ii)$$

Divide equation (i) by (ii)

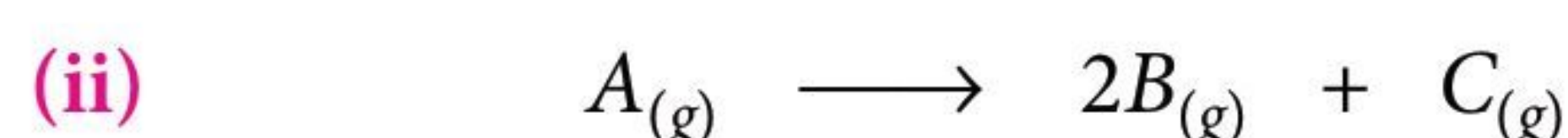
$$\frac{kt_{99\%}}{kt_{90\%}} = \frac{2.303 \log 10^2}{2.303 \log 10} \Rightarrow \frac{t_{99\%}}{t_{90\%}} = \frac{2 \log 10}{\log 10} = 2$$

$$t_{99\%} = 2t_{90\%}$$

OR

$$(i) -\frac{d[A]}{dt} = \frac{1}{2} \frac{d[D]}{dt}$$

$$\frac{d[D]}{dt} = 2 \times 2.8 \times 10^{-2} = 5.6 \times 10^{-2} \text{ M s}^{-1}$$



Initial pressure p_A 0 0

Final pressure $p_A - p$ $2p$ p

Total pressure $= p_A - p + 2p + p = 180 \text{ mm Hg}$

$p_A = 90 \text{ mm Hg}$

Then, $p_A + 2p = 180 \text{ mm Hg}$

$$p = \frac{180 - 90}{2} = 45 \text{ mm Hg}$$

$$k = \frac{2.303}{t} \log \frac{p_A}{p_A - p} = \frac{2.303}{10 \times 60} \log \frac{90}{45} = 1.15 \times 10^{-3} \text{ sec}^{-1}$$

8. (a) There are some substances which at low concentrations exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles.

(b) In multimolecular colloids, the smaller particles aggregate and are held together by van der Waals' force, e.g. sols of gold atoms and sulphur molecules.

(c) The method involves both dispersion and condensation. The intense heat of arc vapourises some of the metal which condenses under cold water.

9. (i) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$:

Diamminechloridonitrito-N-platinum(II)

It is square planar and diamagnetic.

(ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$:

Tetraamminedichloridocobalt(III) chloride

It is octahedral and diamagnetic.

(iii) $\text{Ni}(\text{CO})_4$: Tetracarbonylnickel(0)

It is tetrahedral and diamagnetic.

10. (i) When $t = 20 \text{ min}$, $[R] = 0.289 \text{ mol L}^{-1}$
 $[R]_0 = 0.400 \text{ mol L}^{-1}$

For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

$$\therefore k = \frac{2.303}{20} \log \frac{0.400}{0.289} \Rightarrow k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$\Rightarrow k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$$

$$\Rightarrow k = \frac{2.303}{20} [0.6021 - 0.4609]$$

$$\Rightarrow k = \frac{2.303}{20} \times 0.1412$$

$$\Rightarrow k = 2.303 \times 0.00706 \Rightarrow k = 1.626 \times 10^{-2} \text{ min}^{-1}$$

(ii) Initial rate, i.e., rate of reaction when, $t = 0$

When $t = 0.00 \text{ min}$, $[R] = 0.400 \text{ mol L}^{-1}$

Also, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$$\therefore \text{Initial rate} = k[R] \\ = 1.626 \times 10^{-2} \text{ min}^{-1} \times 0.400 \text{ mol L}^{-1} \\ = 6.504 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$(iii) t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

Here, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$, $[R]_0 = 0.400 \text{ M}$,
 $[R] = 0.350 \text{ M}$

Substituting these values in the equation, we get

$$t = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{0.350}$$

$$= \frac{2.303}{1.626 \times 10^{-2}} [\log 40 - \log 35]$$

$$= 141.635 [1.6021 - 1.5441] = 141.635 \times 0.0580$$

$$= 8.21 \text{ min}$$

11. According to Freundlich adsorption isotherm,

$$\left(\frac{x}{m}\right) = k(p)^{1/n} ; \log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log p$$

On comparing this with equation of straight line, we get,

$$\text{Slope} = \frac{1}{n} = 2$$

$$\text{Intercept} = \log k = 0.4771$$

$$k = \text{antilog}(0.4771) = 2.999 \approx 3$$

$$\therefore \frac{x}{m} = 3(4 \times 10^{-2})^2 = 48 \times 10^{-4}$$

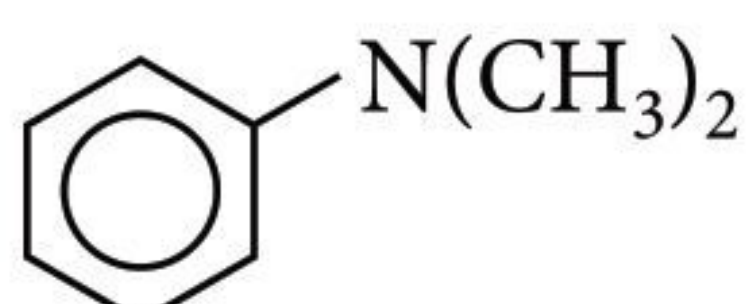
OR

(a) The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherms.

(b) Production of vacuum : Adsorption can be applied to create condition of high vacuum. Vessel which has already been exhausted by vacuum pump is connected to a bulb containing charcoal. The remaining traces of air inspite of low pressure are adsorbed by the charcoal almost completely.

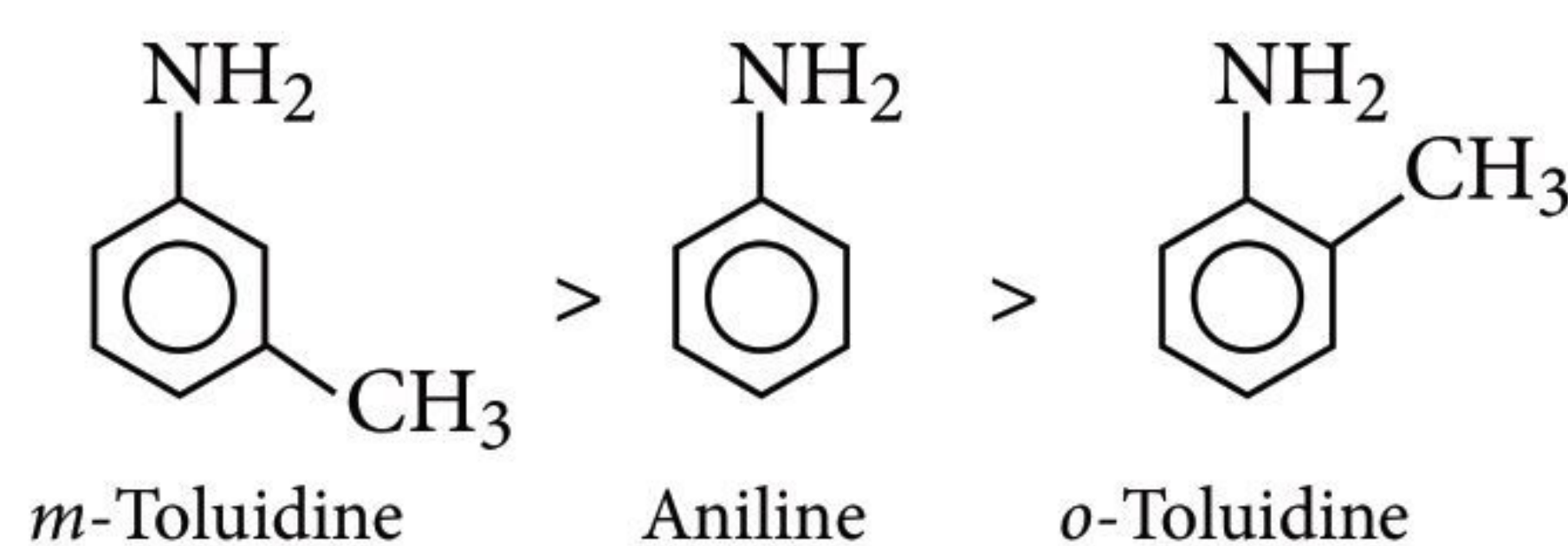
(c) Solution : In true solution, the size of the particles is about 10^{-10} m.

Colloid : In a colloid, the size of the particles is in between 10^{-7} to 10^{-9} m.

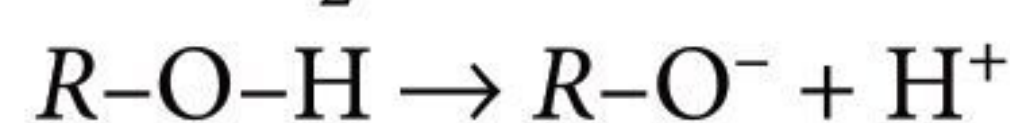
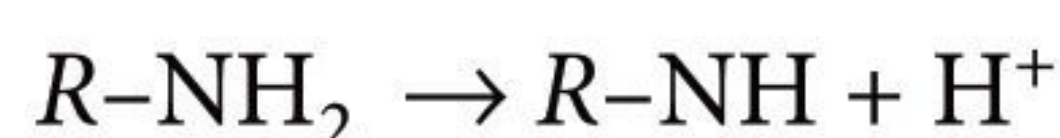
12. (a)  or *N,N*-dimethyl aniline is the stronger base than aniline due to +I-effect of two methyl groups. Hence, it has lowest pK_b value.

(b) In general, electron donating (+R) group which when present on benzene ring ($-\text{NH}_2$, $-\text{OR}$, $-\text{R}$, etc.) at the para position increases the basicity of aniline.

Ortho substituted anilines are weaker bases than aniline due to *ortho* effect.



(c) In alcohols, the hydrogen atom is attached to more electronegative oxygen atom whereas nitrogen of amines is less electronegative. After the loss of H^+ ion, the negative charge is more easily accommodated on oxygen than in case of nitrogen in amines. Hence, amines have lesser tendency to lose H^+ ions, so they are less acidic than alcohols.

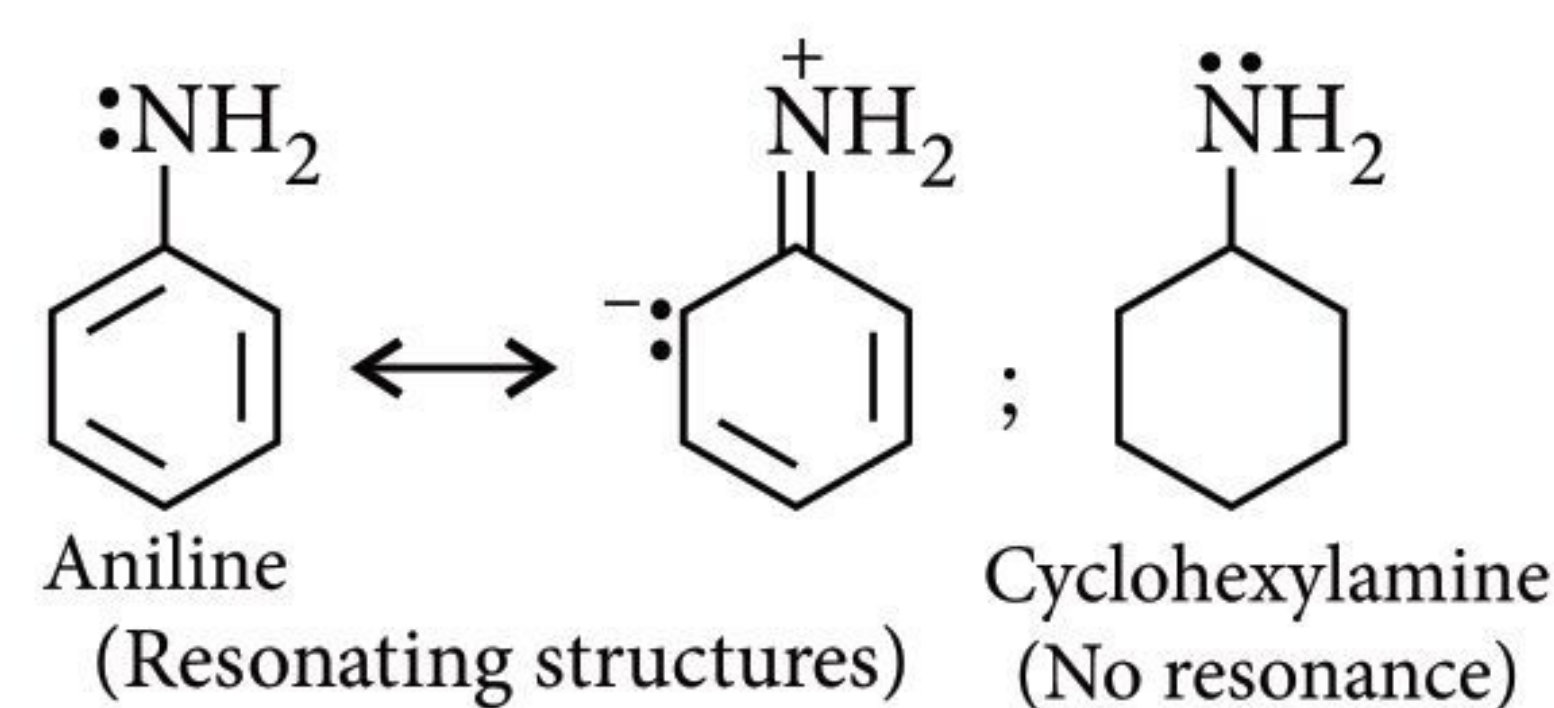


(d) $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

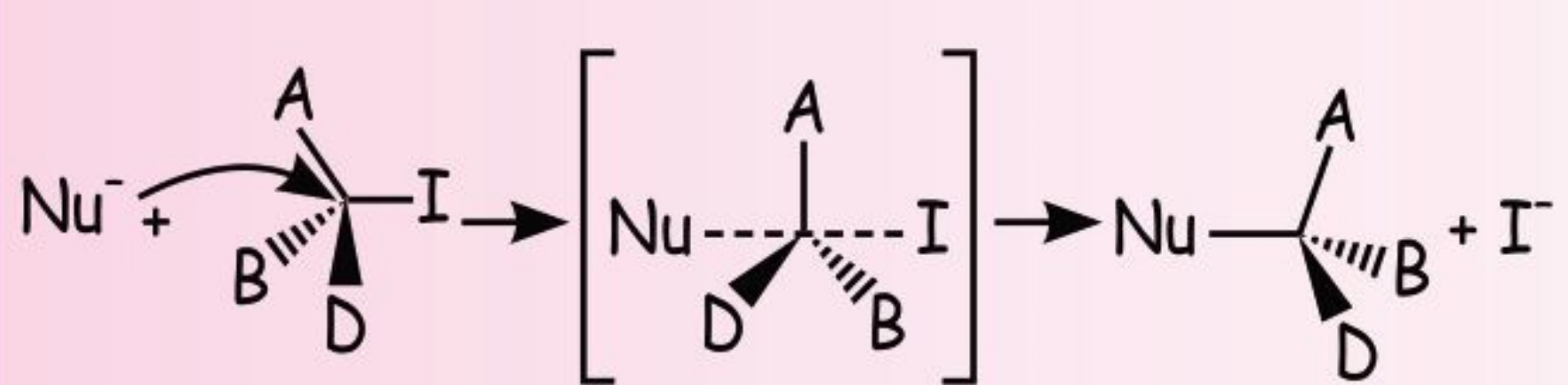
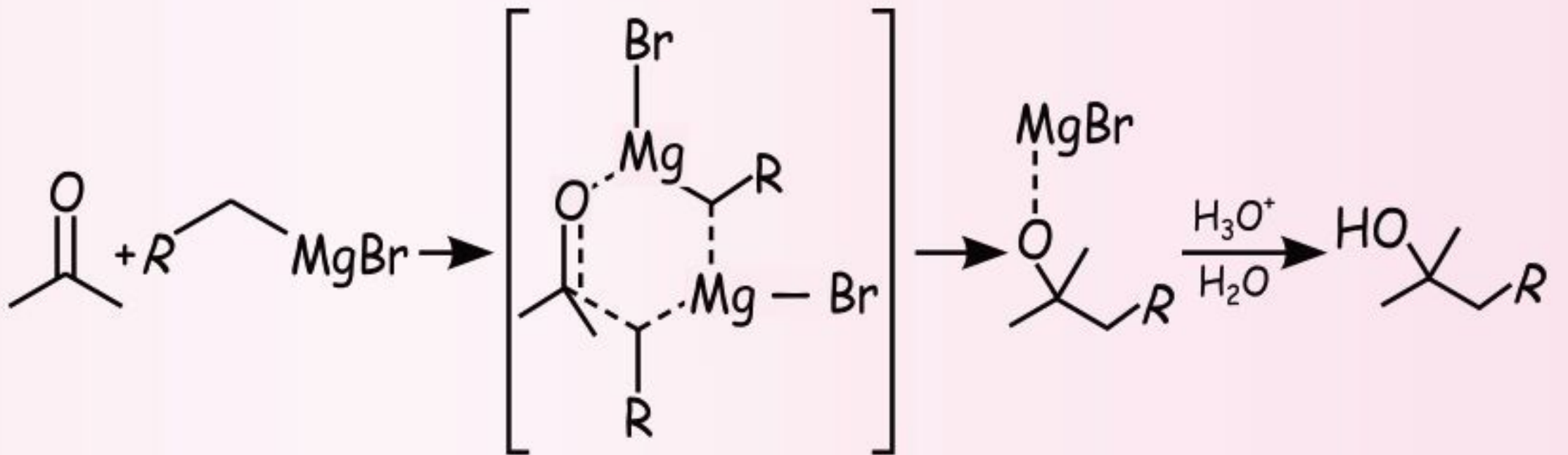

1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

OR

Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is in resonance with by benzene ring. Hence, donor tendency of $-\ddot{\text{N}}\text{H}_2$ group decreases. There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of $-\text{NH}_2$ group. So, cyclohexylamine is a stronger base.



COMIC CAPSULE

Substitution Reaction	Grignard Reaction	My Reaction
		



CONCEPT BOOSTER

Hello students!! I strongly believe that even in this tough pandemic situation you all are fit & fine and so are your family members. You all are always in my prayers. I am always with you to strengthen your concepts in CHEMISTRY because at no cost learning will stop. So guys, this article is all about the concepts of a very important reaction named DIELS-ALDER reactions which more or less comes in the exams very often. This reaction has vast usages in the field of ORGANIC CHEMISTRY and is highly important for competitive exams. So, please go through this article.

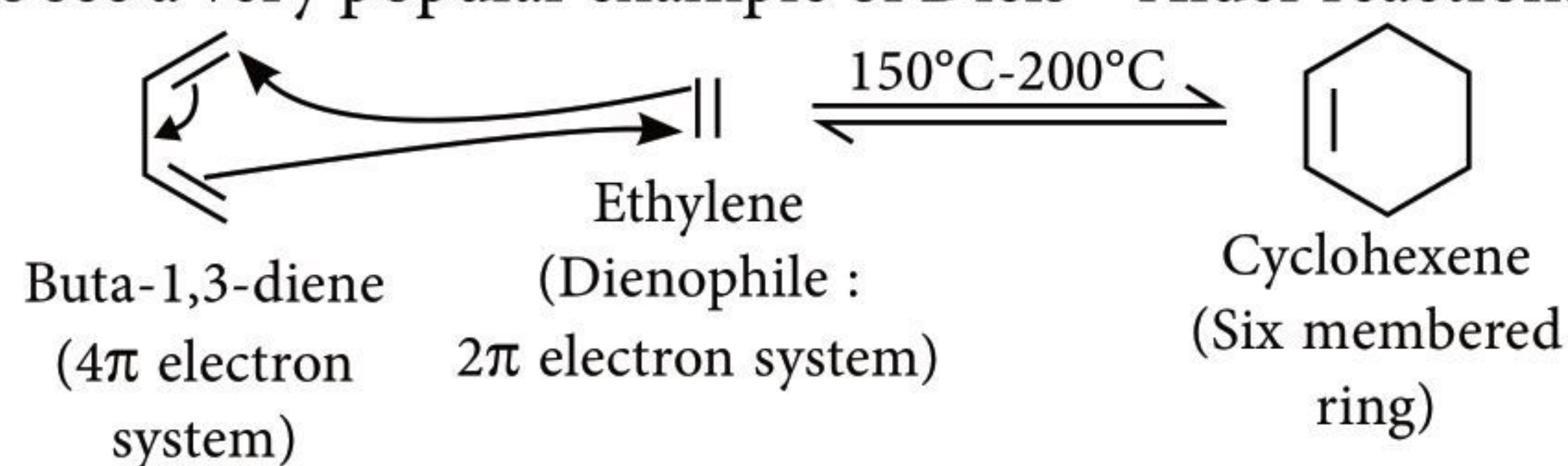
*Arunava Sarkar

SPECIAL TYPE OF ADDITION REACTIONS

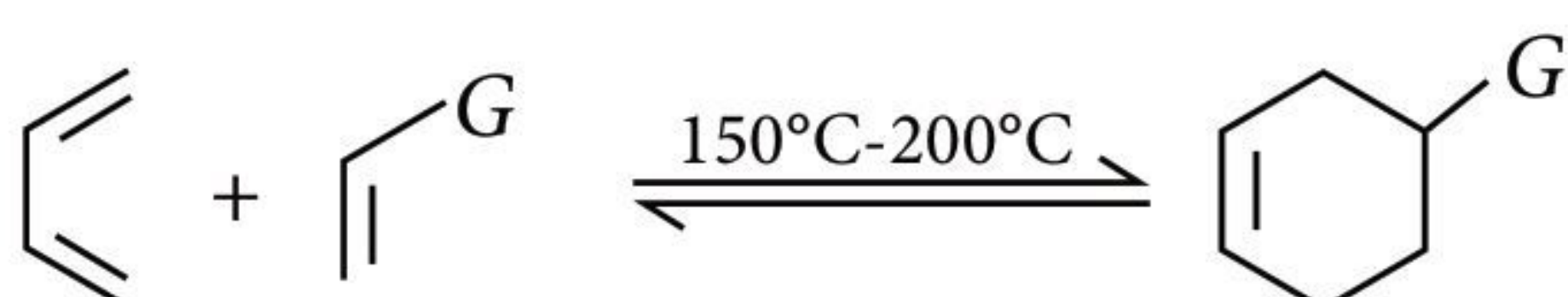
Diels-Alder Reaction

1. This is a thermal (4 + 2) cycloaddition reaction between two compounds where the first one is a 4π electron system containing a diene while the second one is 2π electron system known as dienophile (diene = two double bonds, phile = loving).

The dienophile contains an active multiple bond (specially a double bond *i.e.*, 2π electron system). Let us see a very popular example of Diels – Alder reaction.



The dienophile can even be a substituted one.



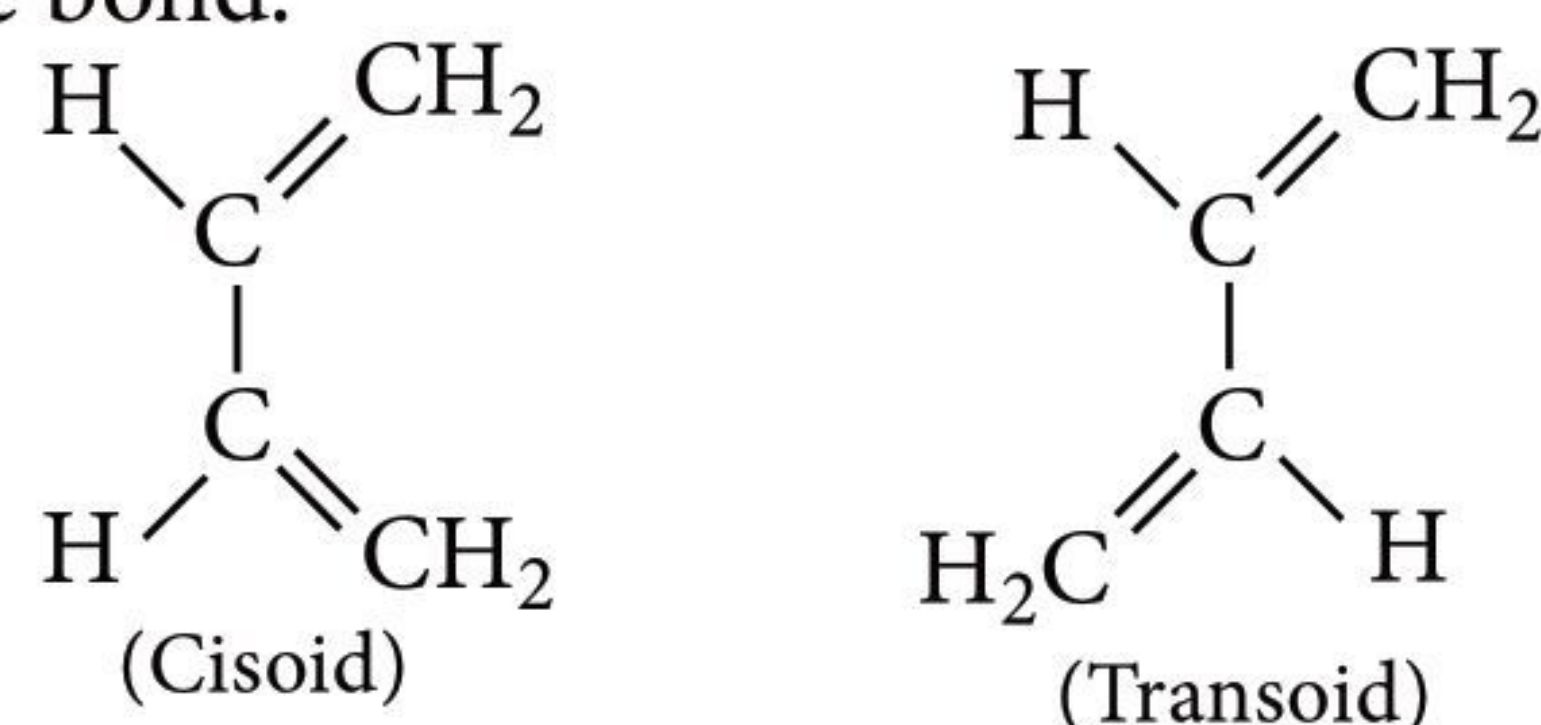
where, G is preferably an electron withdrawing group like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CH}_2\text{Cl}$, $-\text{X}$, $-\text{CH}_2\text{OH}$, etc.

Note : 1 Diels – Alder reaction is reversible in nature.

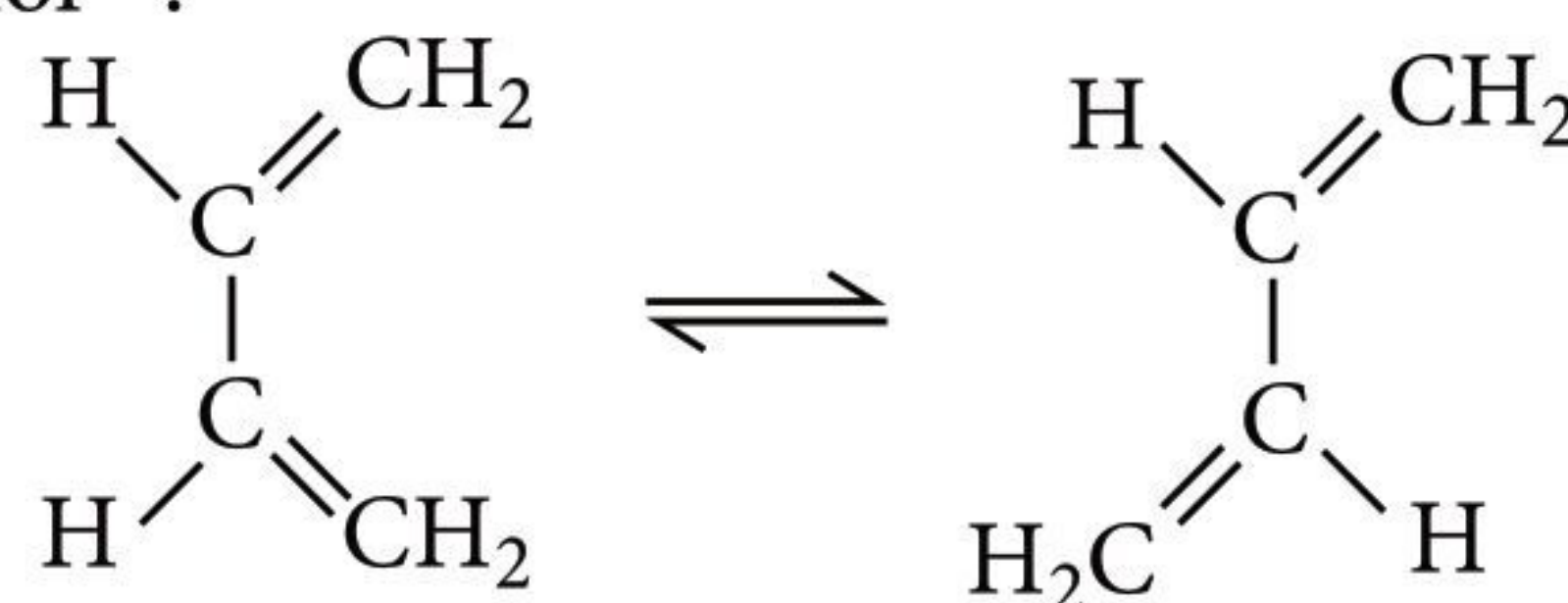
2. The rate of the reaction can be increased if an electron donating group is present on diene. $+I$ and $+R$ effect exerting groups increase the electron supply in the diene system.

On the other hand, dienophile system should be devoid of electrons. If electron withdrawing groups *i.e.*, $-I$ and $-R$ effect exerting groups are attached to this system then the rate enhancement in the Diels – Alder reaction is observed.

3. Diene component for example, buta-1, 3-diene has two major conformations : One is *S-cis* (cisoid) and the another is *S-trans* (transoid). Here, 'S' stands for single bond and the conformation is obtained with respect to the single bond.



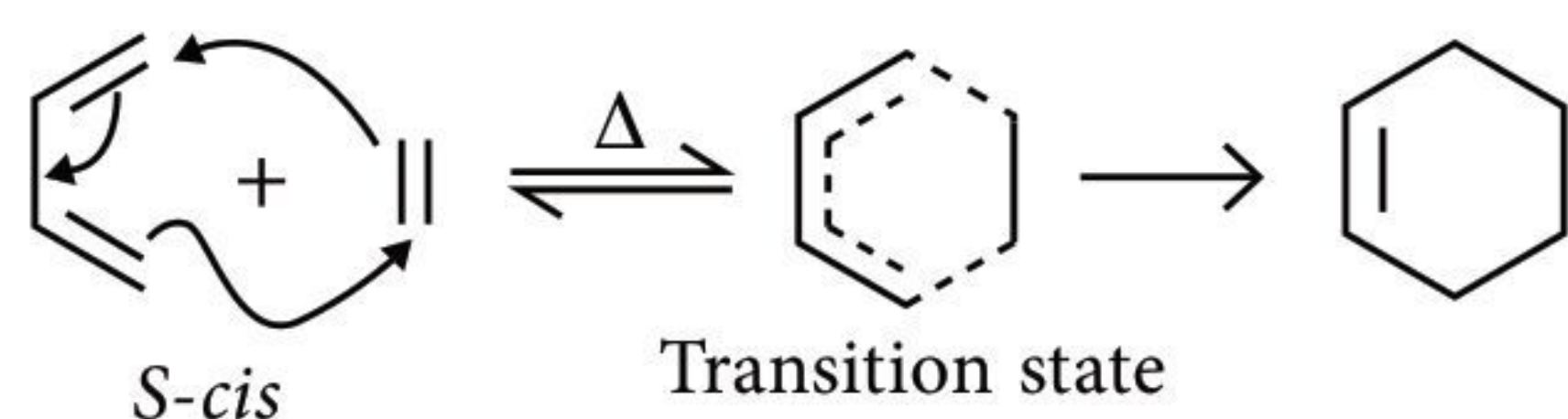
Generally, *S-trans* is energetically more stable than *S-cis* because in case of *S-cis* there is a steric repulsion between the hydrogen atoms. However, *S-cis* conformation is suitable for Diels – Alder reaction as there is a *syn*-periplanarity in *S-cis* conformation whereas *S-trans* is *anti*-periplanar. This is a fact that there is always an equilibrium in between the *S-cis* and *S-trans* conformation as energy barrier is very low *i.e.*, 5 kcal mol^{-1} .



*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

Mechanistic Approach of Diels-Alder Reaction

Diels-Alder reaction is supposed to occur through a concerted path.

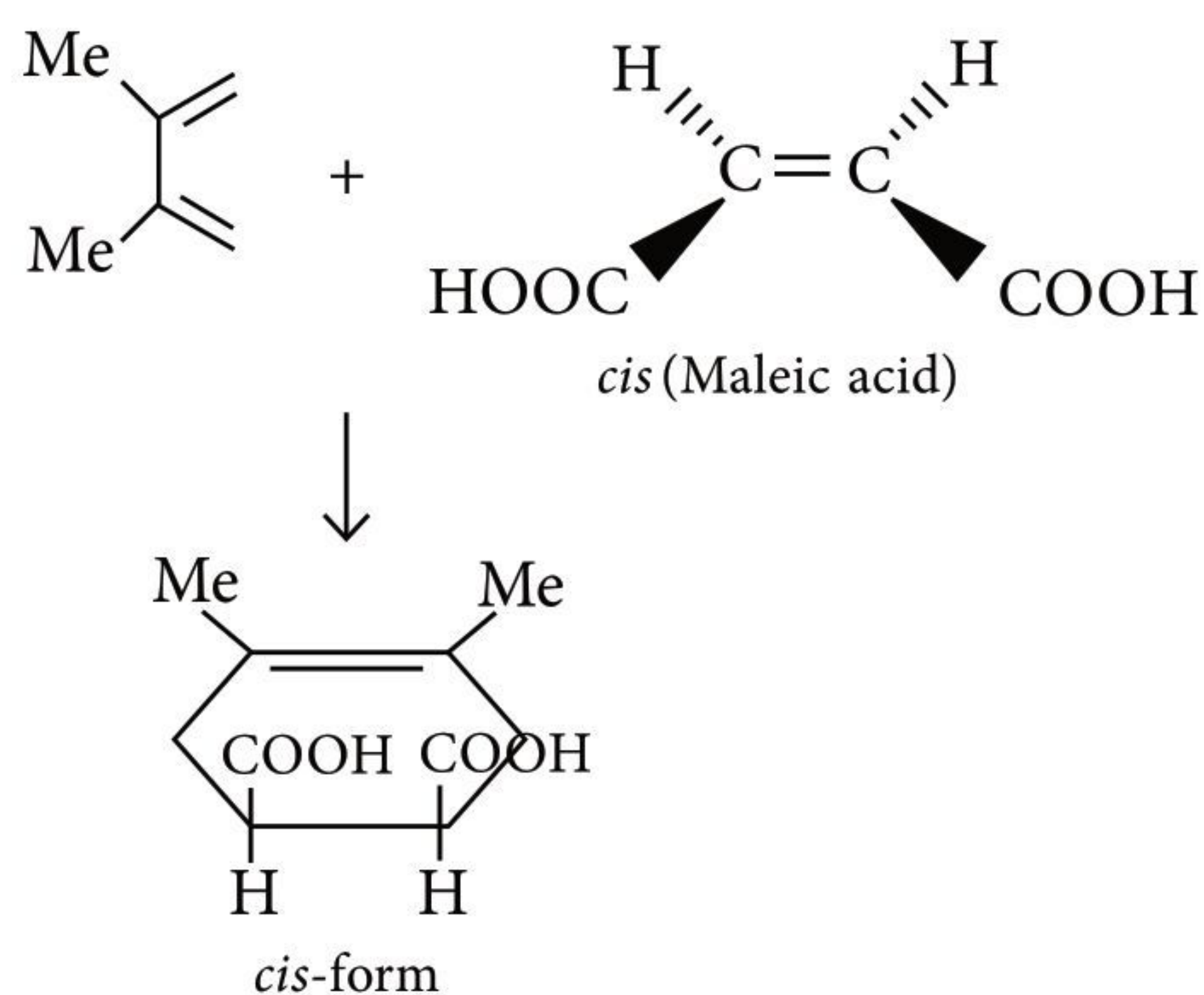


Though, initial amount of *S-cis* conformation is found to be little but it is enough to start the reaction. As already mentioned that there is an equilibrium in between *S-cis* and *S-trans*, therefore, with the loss in the amount of *S-cis* conformation, some amount of *S-trans* converts into *S-cis* and thus the reaction succeeds.

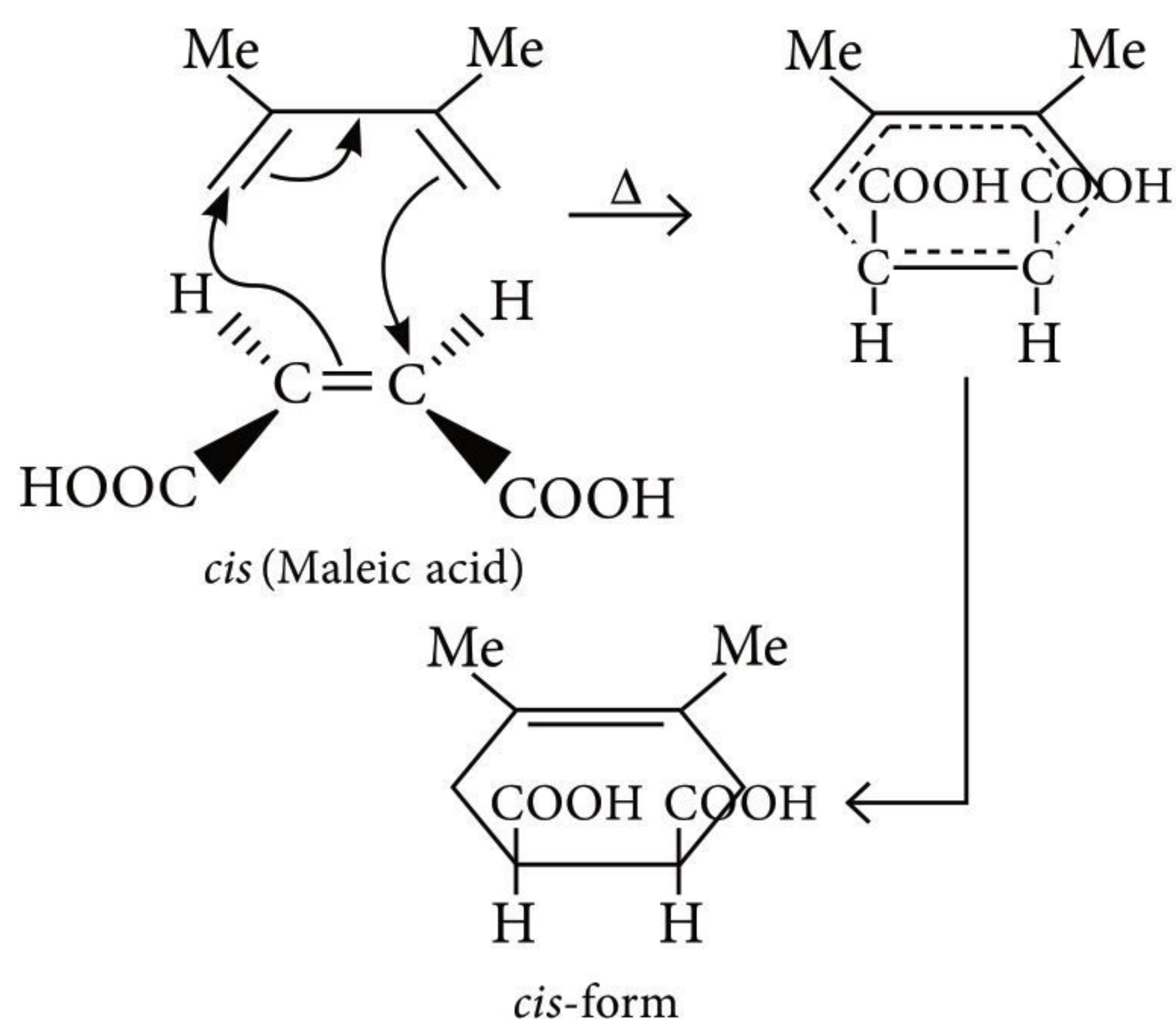
Stereochemistry of Diels—Alder reaction :

Diels—Alder reaction proceeds through concerted path. Therefore, there is retention in the configuration. Moreover, Diels—Alder reaction is stereospecific.

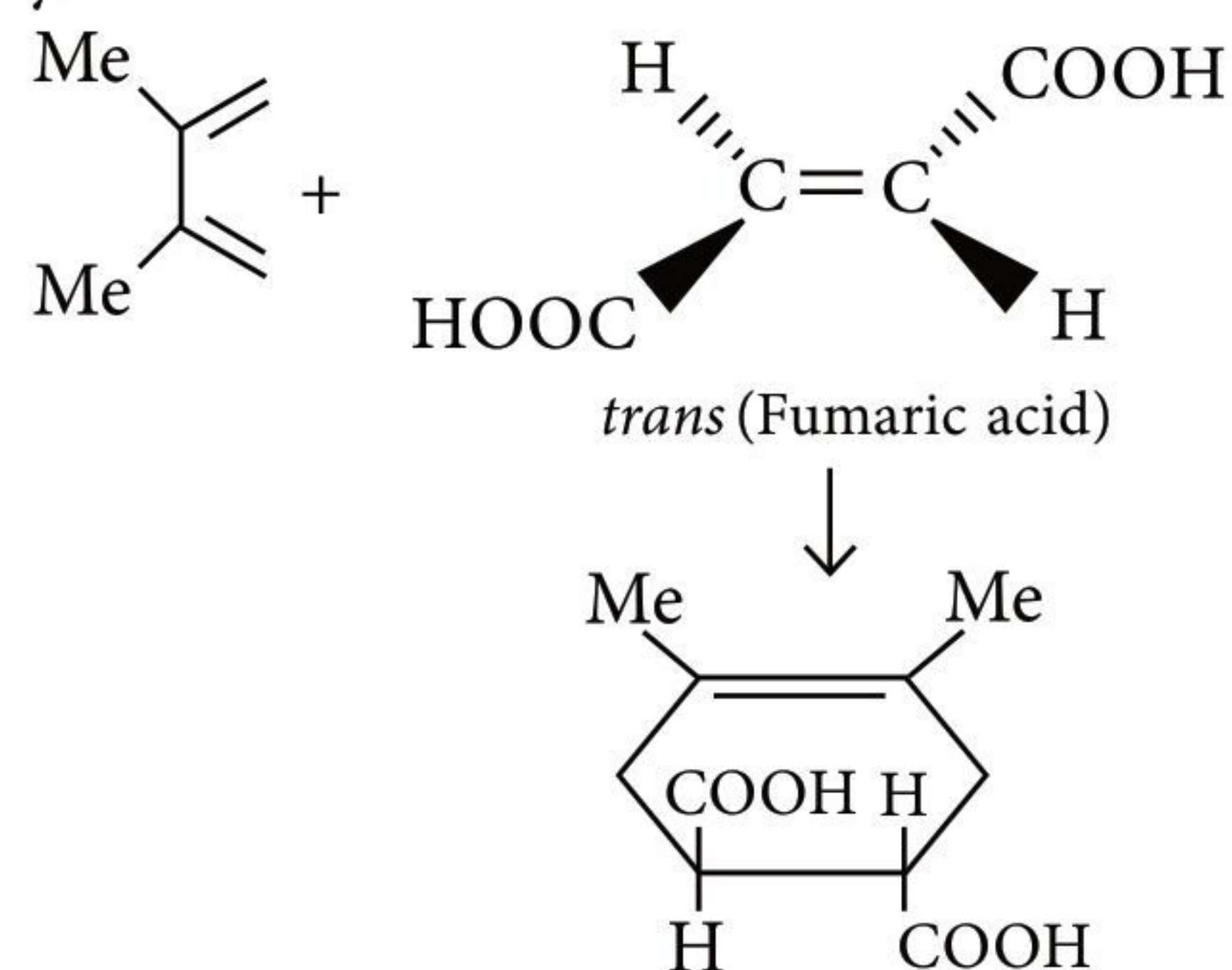
For example,



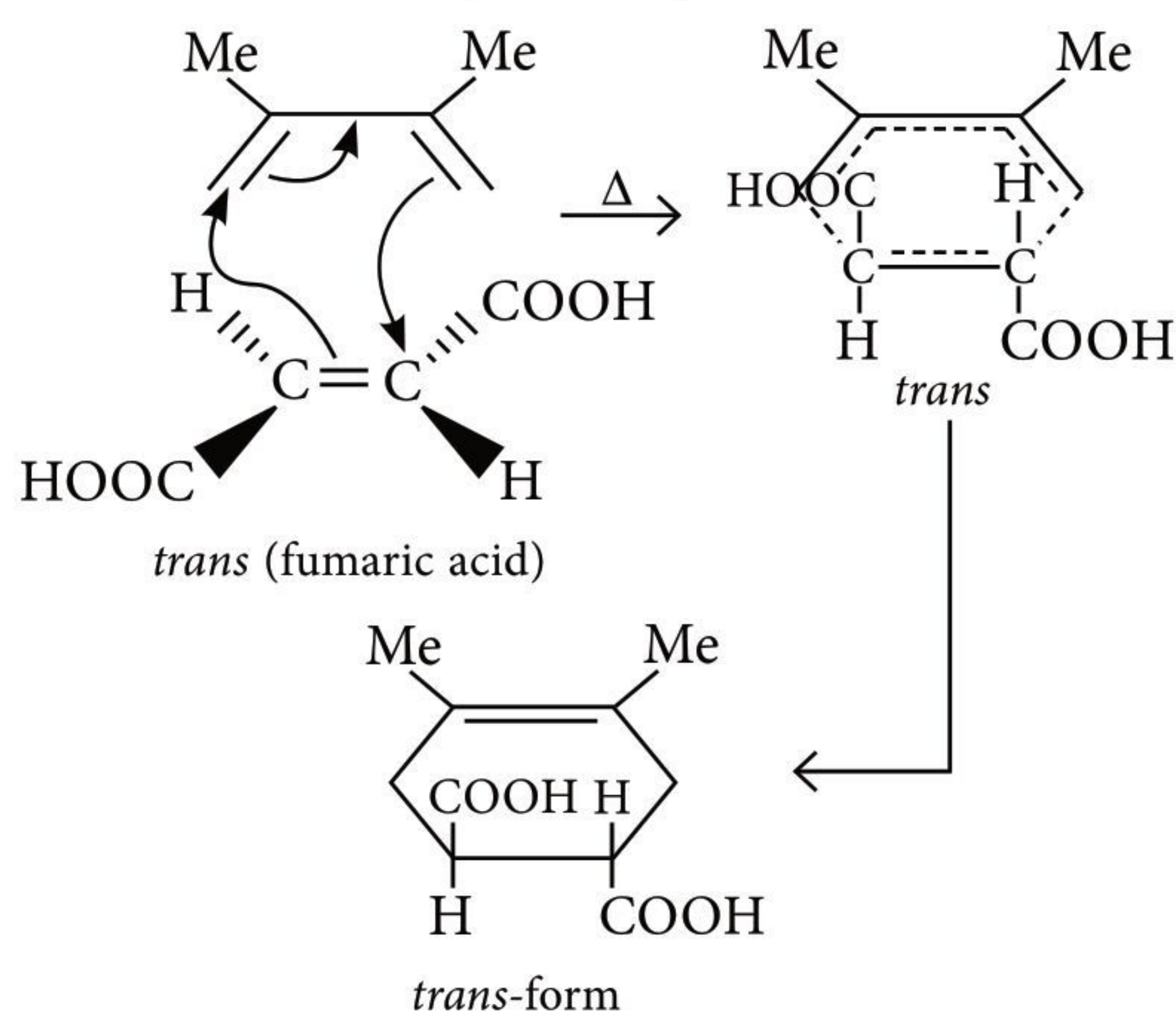
The reaction takes place as given below :



Similarly,



The reaction takes place as given below:



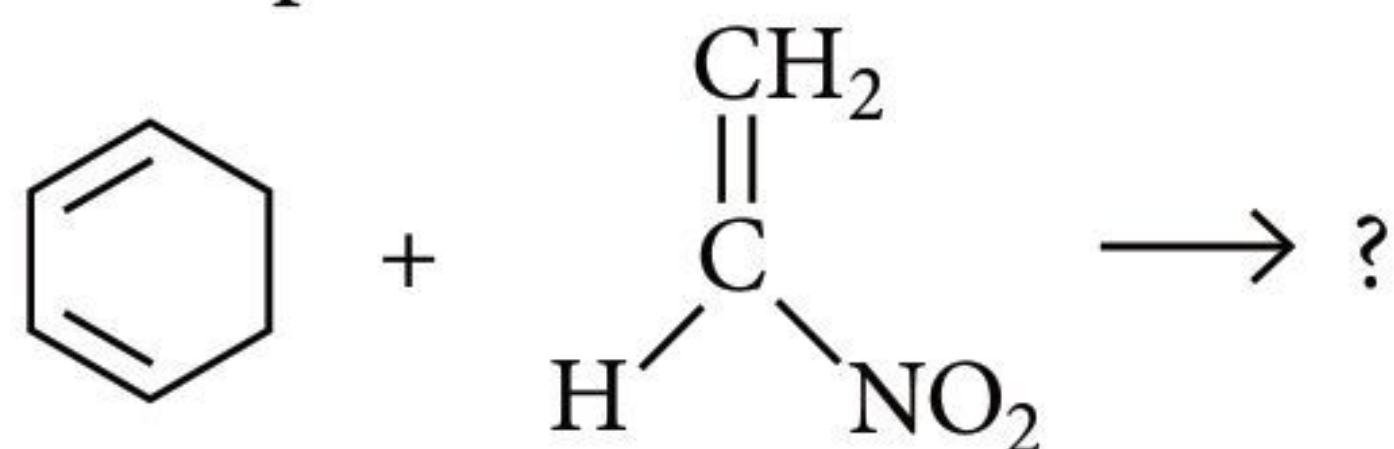
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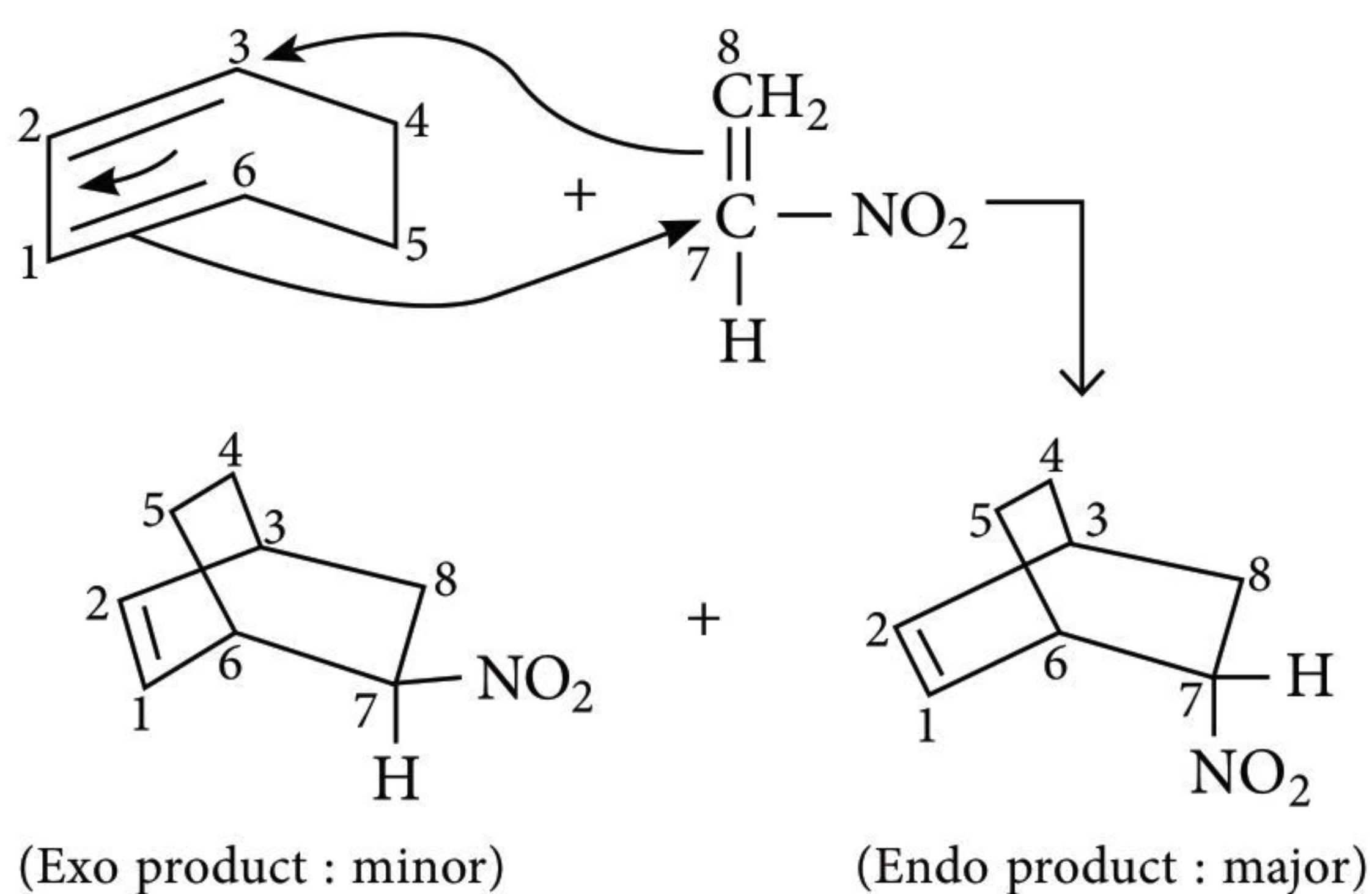
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Exo and Endo Product Formation

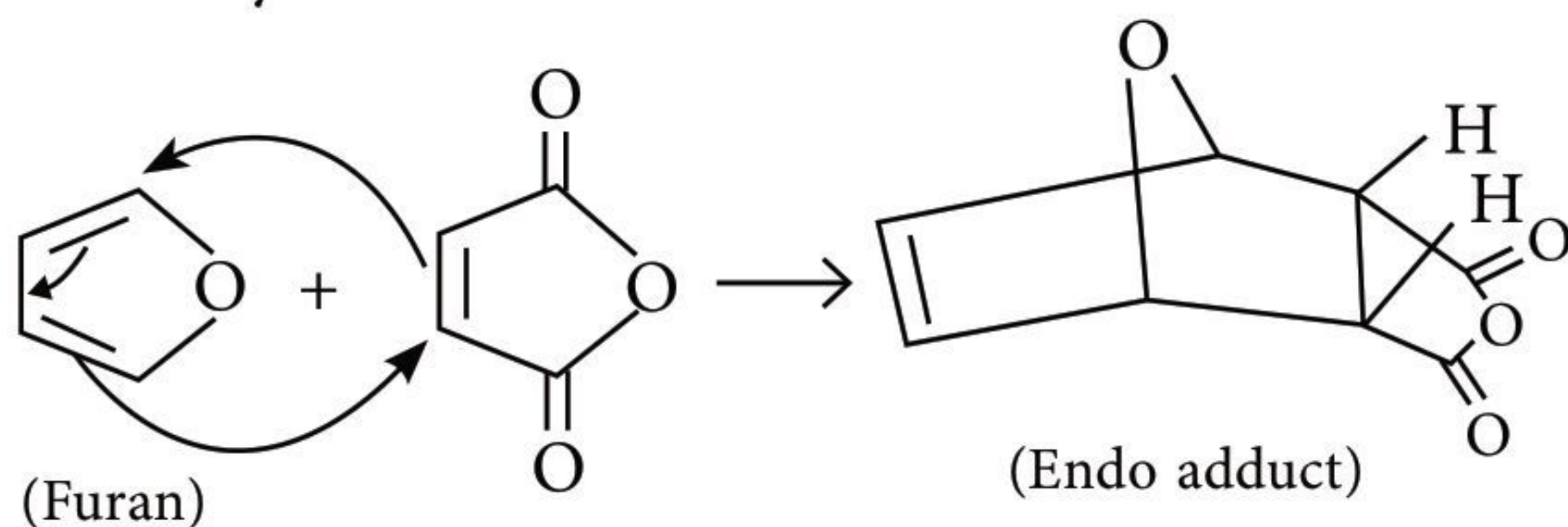
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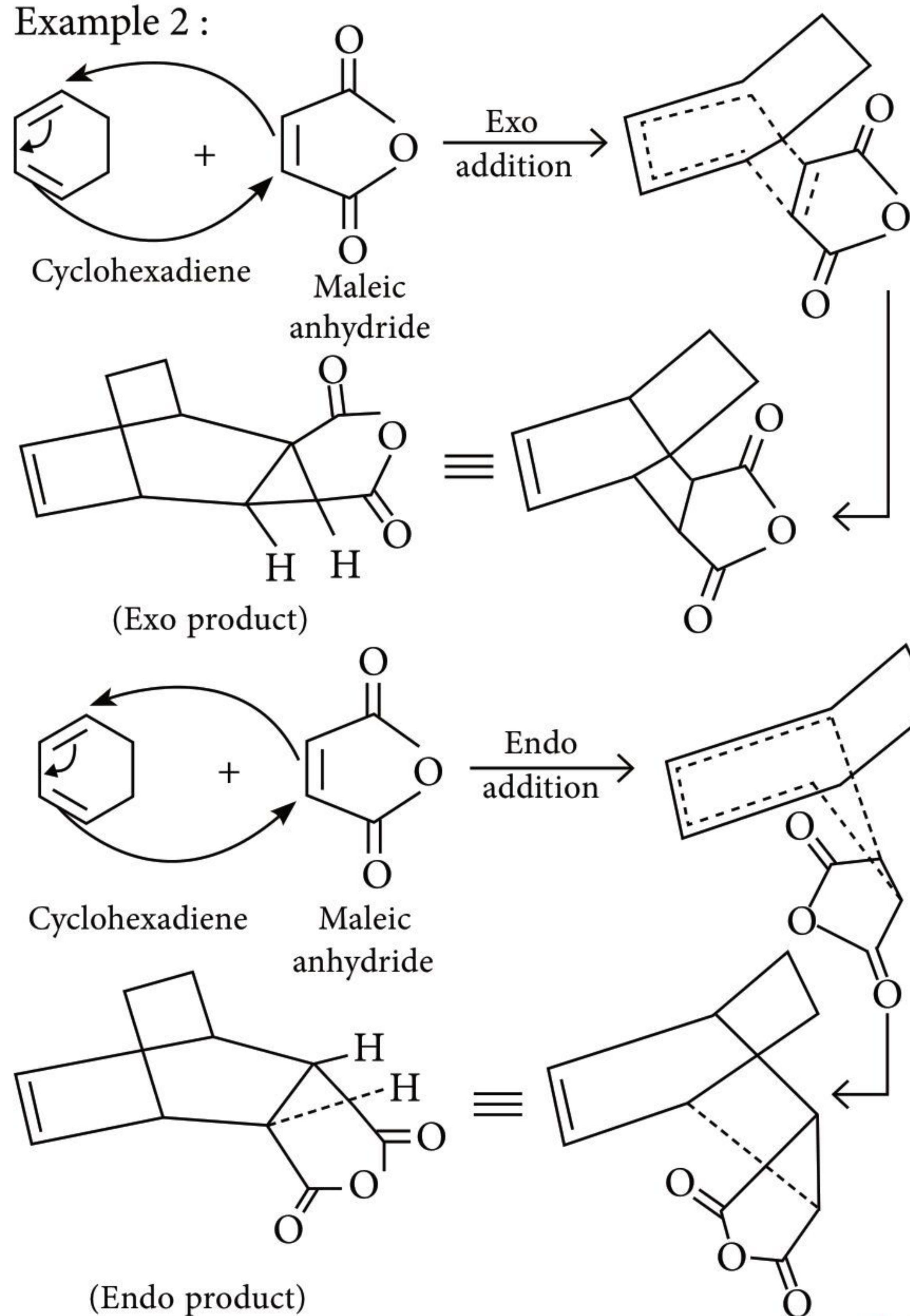
Reaction proceeds as the following manner.



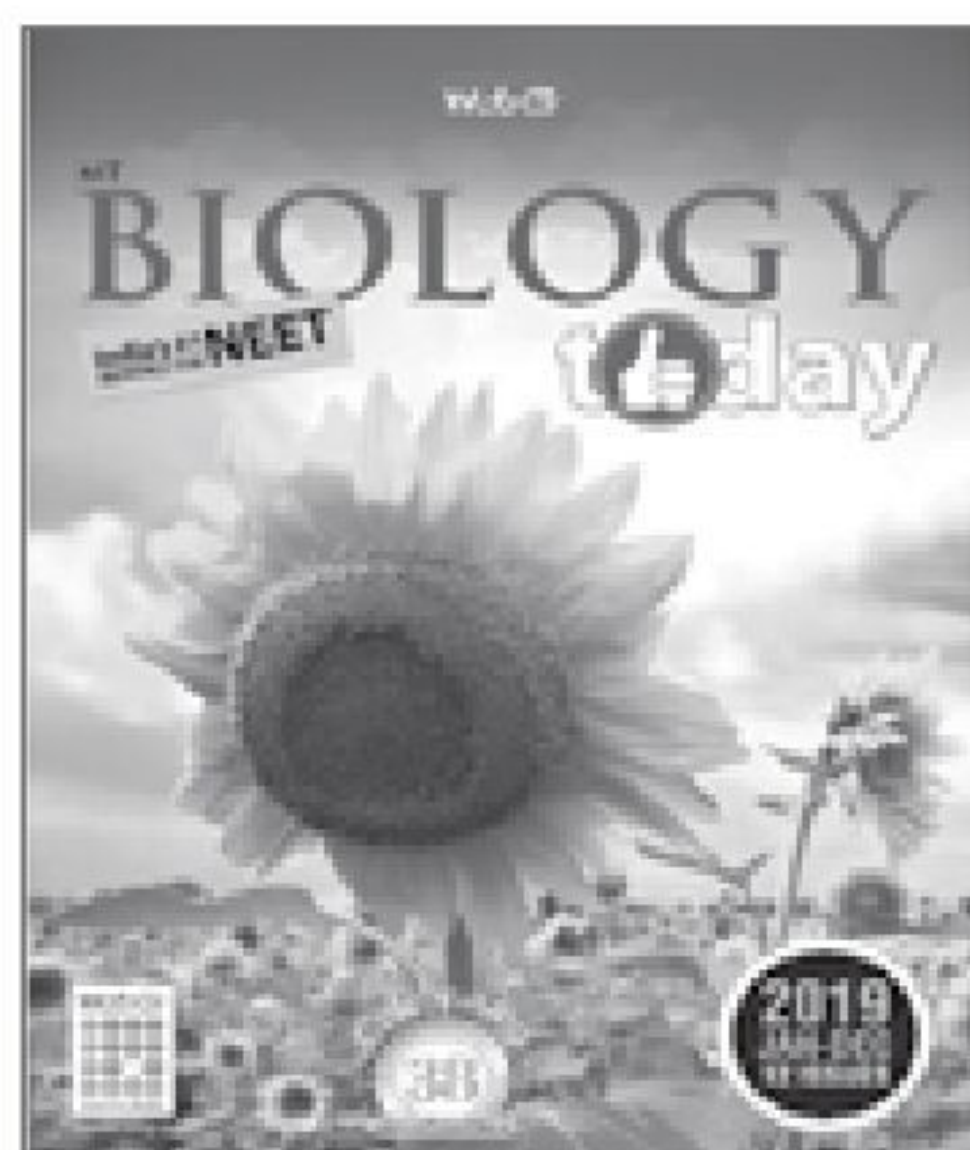
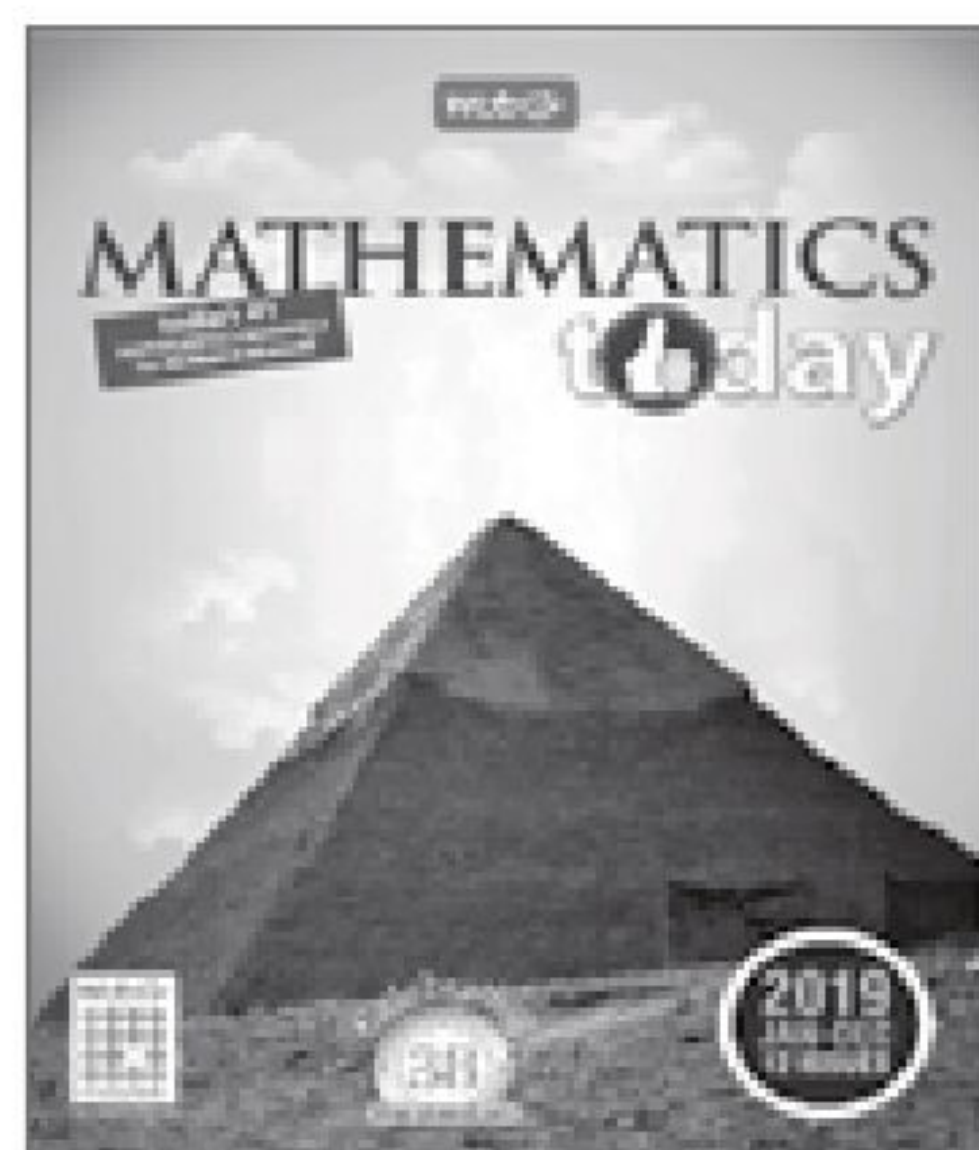
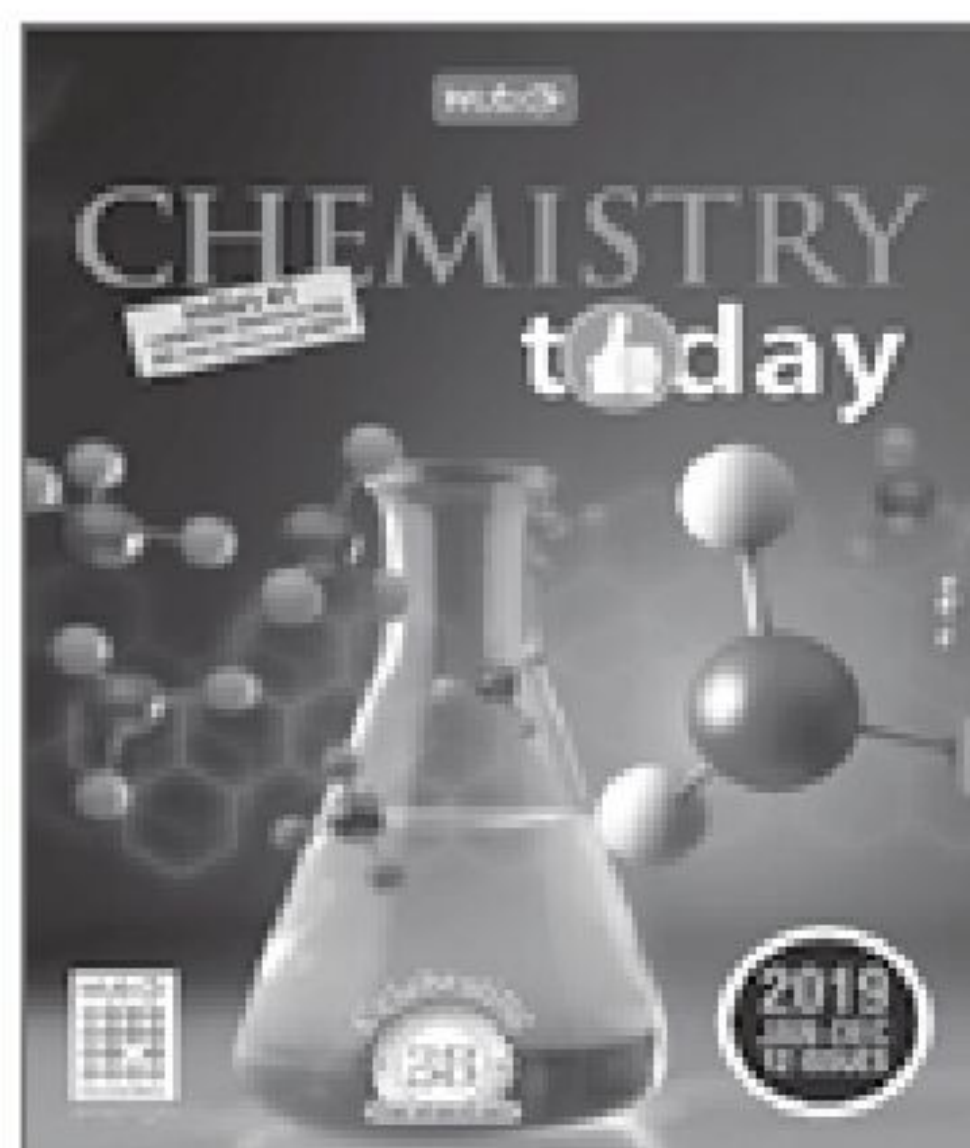
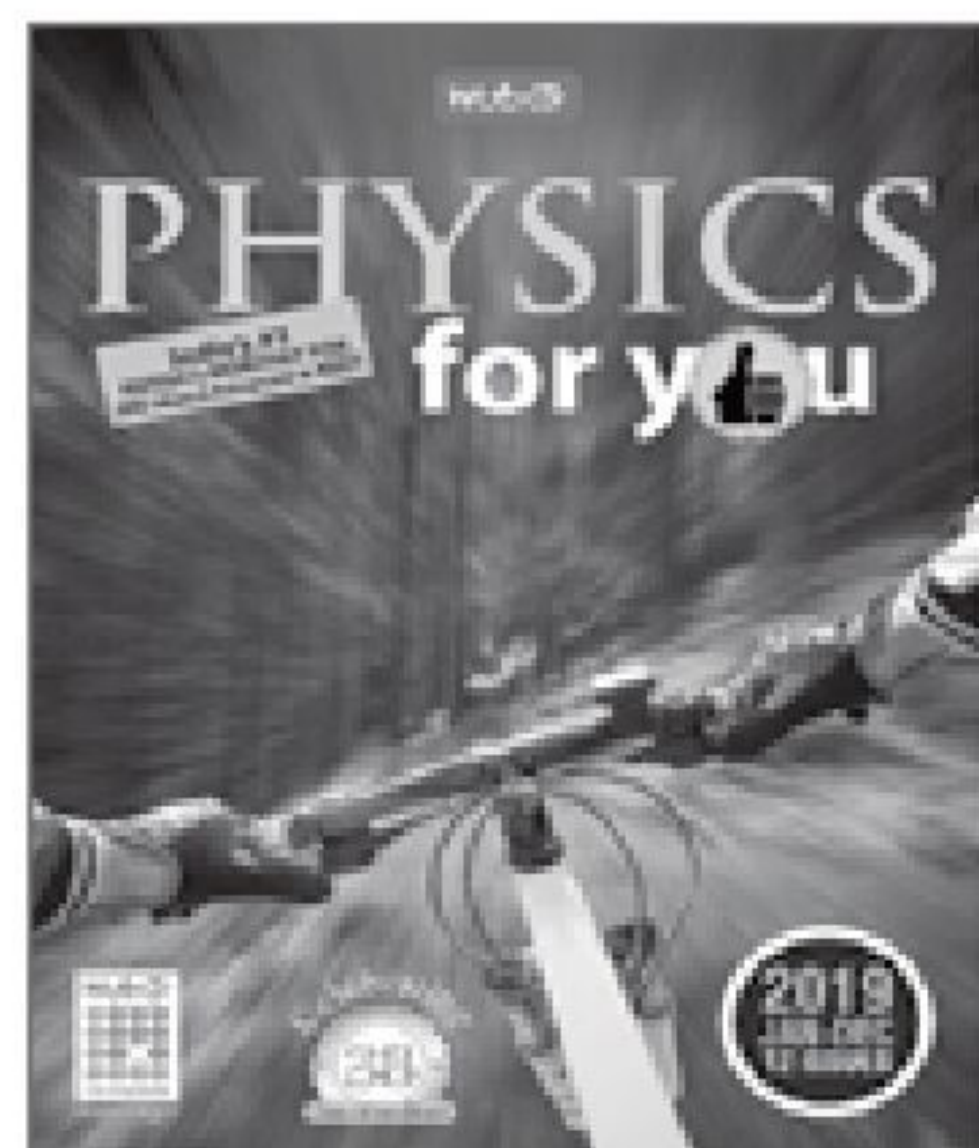
Similarly,



Example 2 :



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ESSENTIALS FOR TERM-II

The *d*- and *f*-Block Elements & Coordination Compounds



The *d*-Block Elements (Transition Elements)

- Transition elements are the elements which lie between most electropositive *s*-block and most electronegative *p*-block elements in the long form of the periodic table. They are called *transition elements* because their properties lie in between those of *s*-block and *p*-block elements.
- General electronic configuration of the transition elements is $(n-1)d^{1-10}ns^{0-2}$ where *n* is the outermost shell.

Electronic Configuration of Some Transition Elements

3 <i>d</i> -Series			4 <i>d</i> -Series			5 <i>d</i> -Series		
Atomic No.	Element	Electronic Configuration	Atomic No.	Element	Electronic Configuration	Atomic No.	Element	Electronic Configuration
21	Sc	[Ar]3 <i>d</i> ¹ 4 <i>s</i> ²	39	Y	[Kr]4 <i>d</i> ¹ 5 <i>s</i> ²	57	La	[Xe]5 <i>d</i> ¹ 6 <i>s</i> ²
22	Ti	[Ar]3 <i>d</i> ² 4 <i>s</i> ²	40	Zr	[Kr]4 <i>d</i> ² 5 <i>s</i> ²	72	Hf	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ² 6 <i>s</i> ²
23	V	[Ar]3 <i>d</i> ³ 4 <i>s</i> ²	41	Nb	[Kr]4 <i>d</i> ⁴ 5 <i>s</i> ¹	73	Ta	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ³ 6 <i>s</i> ²
24	Cr	[Ar]3 <i>d</i> ⁵ 4 <i>s</i> ¹	42	Mo	[Kr]4 <i>d</i> ⁵ 5 <i>s</i> ¹	74	W	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ⁴ 6 <i>s</i> ²
25	Mn	[Ar]3 <i>d</i> ⁵ 4 <i>s</i> ²	43	Tc	[Kr]4 <i>d</i> ⁵ 5 <i>s</i> ²	75	Re	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ⁵ 6 <i>s</i> ²
26	Fe	[Ar]3 <i>d</i> ⁶ 4 <i>s</i> ²	44	Ru	[Kr]4 <i>d</i> ⁷ 5 <i>s</i> ¹	76	Os	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ⁶ 6 <i>s</i> ²
27	Co	[Ar]3 <i>d</i> ⁷ 4 <i>s</i> ²	45	Rh	[Kr]4 <i>d</i> ⁸ 5 <i>s</i> ¹	77	Ir	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ⁷ 6 <i>s</i> ²
28	Ni	[Ar]3 <i>d</i> ⁸ 4 <i>s</i> ²	46	Pd	[Kr]4 <i>d</i> ¹⁰ 5 <i>s</i> ⁰	78	Pt	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ⁹ 6 <i>s</i> ¹
29	Cu	[Ar]3 <i>d</i> ¹⁰ 4 <i>s</i> ¹	47	Ag	[Kr]4 <i>d</i> ¹⁰ 5 <i>s</i> ¹	79	Au	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ¹⁰ 6 <i>s</i> ¹
30	Zn	[Ar]3 <i>d</i> ¹⁰ 4 <i>s</i> ²	48	Cd	[Kr]4 <i>d</i> ¹⁰ 5 <i>s</i> ²	80	Hg	[Xe]4 <i>f</i> ¹⁴ 5 <i>d</i> ¹⁰ 6 <i>s</i> ²

General Properties of Transition Elements

- All transition elements are metals as they possess one or two electrons in their outermost shell.
- They possess metallic lustre and are hard, ductile, malleable and good conductors of heat and electricity.
- Strong metallic bonding due to greater nuclear charge and large number of valence electrons results in high-density hard solid metals (except mercury which is liquid).
- Presence of unpaired *d*-electrons favours covalent bond formation, hence greater the number of unpaired *d*-electrons, more is the number of covalent bonds resulting in hard metals.
- The atomic and ionic radii of *d*-block elements are smaller than their corresponding *s*-block elements.
- The atomic radii of the elements of 3*d* series show a gradual decrease from Sc to Mn and become almost constant after that.
- The decrease in atomic radii in the first five elements is due to increasing '*effective nuclear charge*' with increase in atomic number. The *ns*-electrons are pulled inwards, decreasing the size. As the number of *d*-electrons increases, there is an increase in the screening effect, thus the attractive effect of nuclear charge gets balanced and the size of atoms remains almost same. The increase in atomic radii at the end of the series can be explained due to inter-electronic repulsions among the $(n-1)d$ electrons.

- ◆ Ionic radii (e.g., M^{2+}) show the same trend for the same oxidation state. The ionic radius will decrease with increase in charge on the metal ion.
- ◆ **Ionisation energies** : The ionisation energy increases with the increase in the atomic number but not in regular manner. The *I.E.* of *5d*-elements are higher than those of the *4d*- and *3d*-elements due to greater effective nuclear charge which in turn is due to poor shielding of nucleus by *4f*-electrons.
- ◆ **Electrode potential (E°)** : For the *3d*-transition metals the $E^\circ(M^{2+}/M)$ values (in volts) are :

V	Cr	Mn	Fe	Co	Ni	Cu
-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	0.34

 The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper *3d*-elements are good reducing agents but weaker than *s*-block elements.
- ◆ **Variable oxidation states** : All transition elements except the first and the last member in each series show variable oxidation states. This is because the difference of energy in the $(n-1)d$ - and *ns*-orbitals is very less.
- ◆ **High melting and boiling point** : These metals have very high melting and boiling points due to stronger metallic bonding. The melting point of the transition elements first rise to a maximum and then fall as the atomic number increases.
- ◆ **Complex formation** : Transition elements form large number of complexes due to presence of vacant *d*-orbitals, small size and high charge density.
- ◆ **Magnetic properties** : Magnetic moment is determined by number of unpaired electrons (*n*) and is calculated using spin-only formula *i.e.*, $\mu = \sqrt{n(n+2)}$ B.M.
- ◆ **Alloy formation** : They form alloys due to similar atomic radii.
- ◆ **Interstitial compounds** : They form interstitial compounds due to empty spaces in their lattices in which small atoms can be accommodated.
- ◆ **Formation of coloured ions** : Most compounds of transition metals are coloured in contrast to compounds of *s*- and *p*-block elements.
- ◆ The transition metal ions absorb only that portion of incident light whose wavelength lies between 4000 Å and 7000 Å (visible region).
- ◆ In complex compounds, the colour of the absorbed light also depends on the nature of ligands.
- ◆ Another important reason of colour in transition metals with incomplete *d* sub-shells is the excitation

of electrons from one *d* level to another *d* level of higher energy.

- ◆ The five *d*-orbitals are generally degenerate in a gaseous atom and non degenerate in presence of other ions in 'solution' or compound. Depending on the difference in the energies of the *d*-orbitals, light is absorbed in the visible region, to promote electrons, this gives rise to colour of the ions.
- ◆ Transition metal atoms or ions with completely filled (Zn) or completely empty (Sc^{3+}) *d* sub-shells are white, since no $d \rightarrow d$ transition can occur.

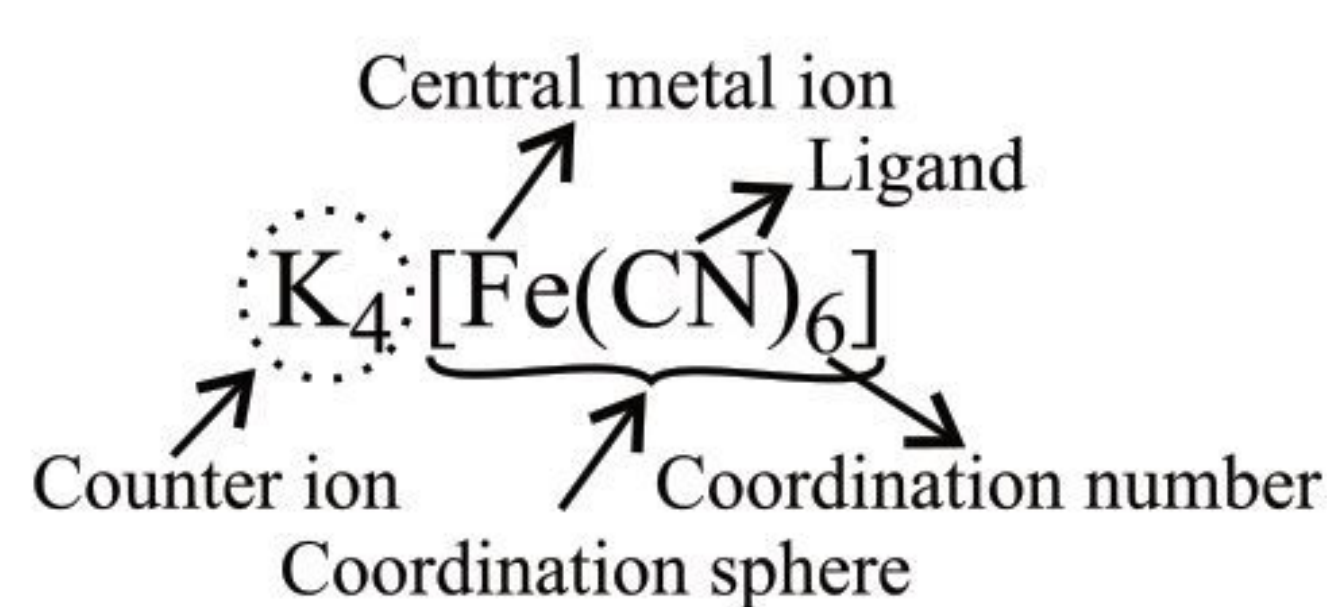
The Inner Transition Elements (*f*-Block)

- ◆ The *f*-block consists of two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).
- ◆ **Lanthanoids** : Last electron enters one of the *4f*-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- ◆ **General electronic configuration** : $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$
- ◆ Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or fully-filled *f*-subshell, e.g., Ce^{4+} acts as an oxidising agent and gets reduced to Ce^{3+} . Eu^{2+} , Yb^{2+} act as strong reducing agents and get oxidised to Eu^{3+} and Yb^{3+} .
- ◆ **Lanthanoid contraction** : In lanthanoid series, with increasing atomic number, there is progressive decrease in atomic/ionic radii (M^{3+} ions) from La^{3+} to Lu^{3+} . Lanthanoid contraction occurs due to addition of new electrons into *f*-subshell and imperfect shielding of one electron by another in the *f*-orbitals, there is greater effect of increased nuclear charge than screening effect hence contraction in size occurs.

Coordination Compounds

- ◆ **Coordination number (C.N.)** : The total number of coordinate bonds through which the central metal atom or ion is attached with ligands is known as coordination number. Examples : $[\text{Ag}(\text{CN})_2]^-$: C.N. = 2, $[\text{Cu}(\text{NH}_3)_4]^{2+}$: C.N. = 4, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$: C.N. = 6
- ◆ **Coordination sphere** : The central atom and the ligands which are directly attached are collectively known as coordination sphere. It is non-ionisable and written enclosed in square brackets. The ionisable groups are written outside the brackets. Example :

$$[\text{Cu}(\text{NH}_3)_4] \text{SO}_4 \rightleftharpoons \underset{\text{Coordination sphere}}{[\text{Cu}(\text{NH}_3)_4]^{2+}} + \underset{\text{Ionisable group}}{\text{SO}_4^{2-}}$$



Rules for IUPAC Nomenclature

- ◆ Cation is named first followed by anion.
- ◆ Non-ionic compounds are given one word name.
- ◆ **Naming of ligands :**
 - Ligands are named first and central atom last.
 - Ligands are named in alphabetical order.
 - Neutral ligands are named as it is as the molecule's name (except aqua and amine).
 - Anionic ligands are named by adding -o to the stem of the name (chloride becomes chlorido).
 - If there are several ligands of the same type, the prefixes like di, tetra, penta and hexa are used to indicate the number of ligands of that type.
- ◆ In a complex, the name of the central metal atom is followed by its oxidation number in roman numerals in parentheses.
- ◆ Names of complex cations and neutral molecules have no distinguishing termination while names of the anionic complexes end in *ate*.
- ◆ In case of bridging ligand the prefix μ is written before the name of the ligand.

Valence Bond Theory

- ◆ It was developed by Pauling. The brief points are the following:

Applications of VBT to some complexes

S. No.	Atom/ion Complex	Configuration	Oxidation State of Metal	Hybridisation and Geometry	No. of Unpaired Electrons	Magnetic behaviour
1.	$\text{Ni}^{2+} (d^8)$	$3d$ $4s$ $4p$ 	+2		2	Paramagnetic
	$[\text{NiCl}_4]^{2-}$		+2	sp^3 , Tetrahedral	2	Paramagnetic
	$[\text{Ni}(\text{CN})_4]^{2-}$		+2	dsp^2 , Square planar	0	Diamagnetic
2.	$\text{Mn}^{2+} (d^5)$	$3d$ $4s$ $4p$ 	+2		5	Paramagnetic
	$[\text{Mn}(\text{CN})_6]^{4-}$		+2	d^2sp^3 , Octahedral	1	Paramagnetic
	$[\text{MnCl}_4]^{2-}$		+2	sp^3 , Tetrahedral	5	Paramagnetic

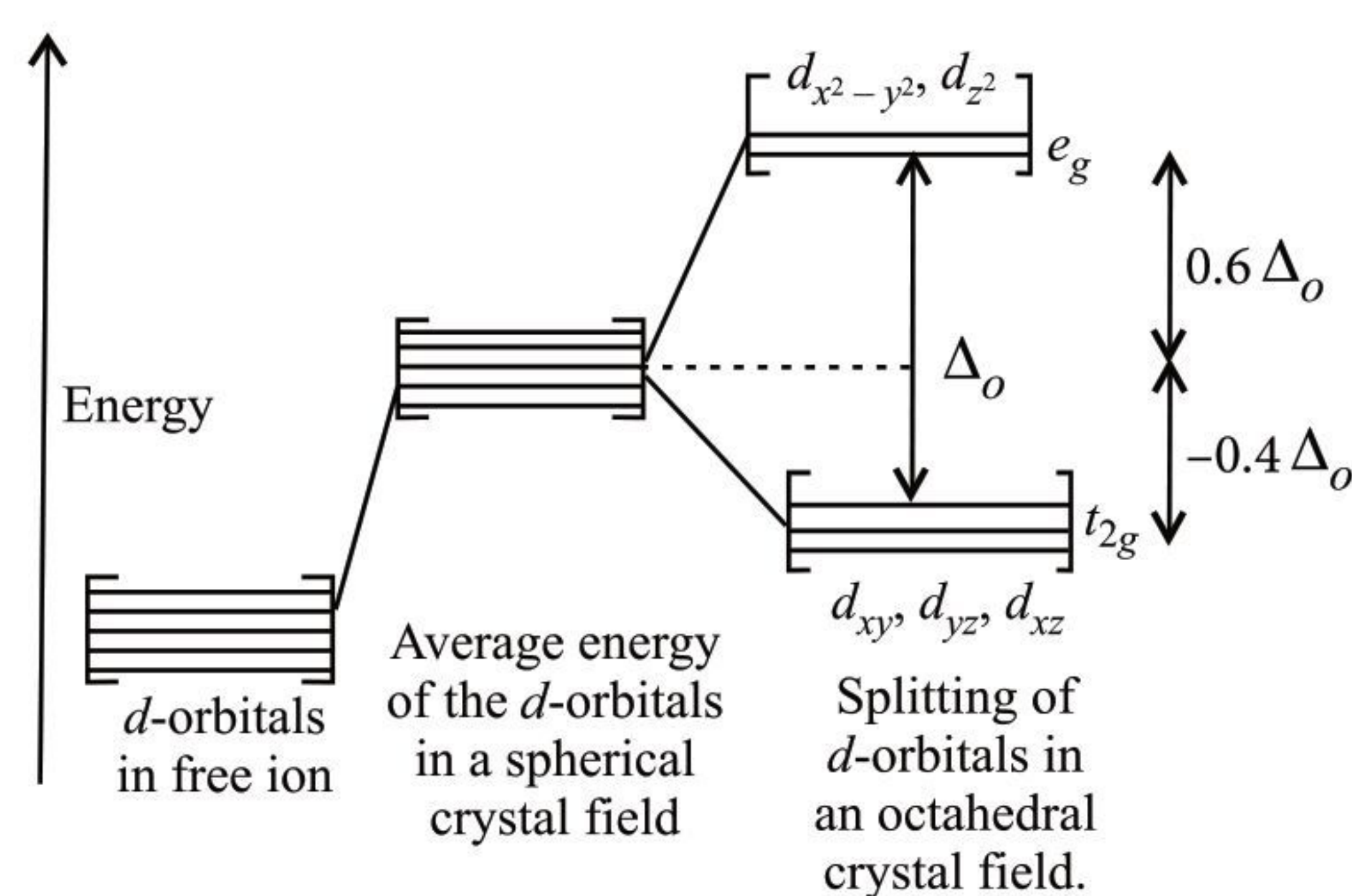
- A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of co-ordinate bonds with the ligands.
- Central metal ion can use appropriate number of s -, p - or d -orbitals for hybridisation depending upon total number of ligands.
- Outer orbital complex (uses outer nd orbitals), high spin complex.
Inner orbital complex [uses inner $(n - 1)d$ orbitals], low spin complex.
- ◆ **Magnetic properties :**
 - Low spin complexes are diamagnetic (generally).
 - High spin complexes are paramagnetic.
 - Paramagnetism \propto No. of unpaired electrons.
 - Magnetic moment $= \sqrt{n(n+2)}$ B.M.
(where n = number of unpaired electrons)
- ◆ **Limitations of VBT**
It fails to
 - give quantitative interpretation of magnetic data.
 - explain the colour exhibited by coordination compounds.
 - give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
 - make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
 - distinguish between weak and strong field ligands.

3.	$\text{Cu}^{2+} (d^9)$	$\begin{array}{c} 3d \quad 4s \quad 4p \\ \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \quad \square \quad \square \end{array}$	+2		1	Paramagnetic
	$[\text{CuCl}_4]^{2-}$	$\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \quad \underbrace{\square \quad \square \quad \square \quad \square}_{sp^3} \end{array}$	+2	sp^3 , Tetrahedral	1	Paramagnetic
	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \quad \underbrace{\square \quad \square \quad \square \quad \square}_{dsp^2} \\ \text{One electron is shifted from } 3d \text{ to } 4p\text{-orbital} \end{array}$	+2	dsp^2 , Square planar	1	Paramagnetic
4.	$\text{Fe}^0 (d^6 s^2)$	$\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \quad \uparrow\downarrow \quad \square \end{array}$	0		4	Paramagnetic
	$[\text{Fe}(\text{CO})_5]$	$\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \quad \underbrace{\square \quad \square \quad \square \quad \square}_{dsp^3} \\ \text{Rearrangement} \end{array}$	0	dsp^3 , Trigonal bipyramidal	0	Diamagnetic

Crystal Field Theory

◆ It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength.

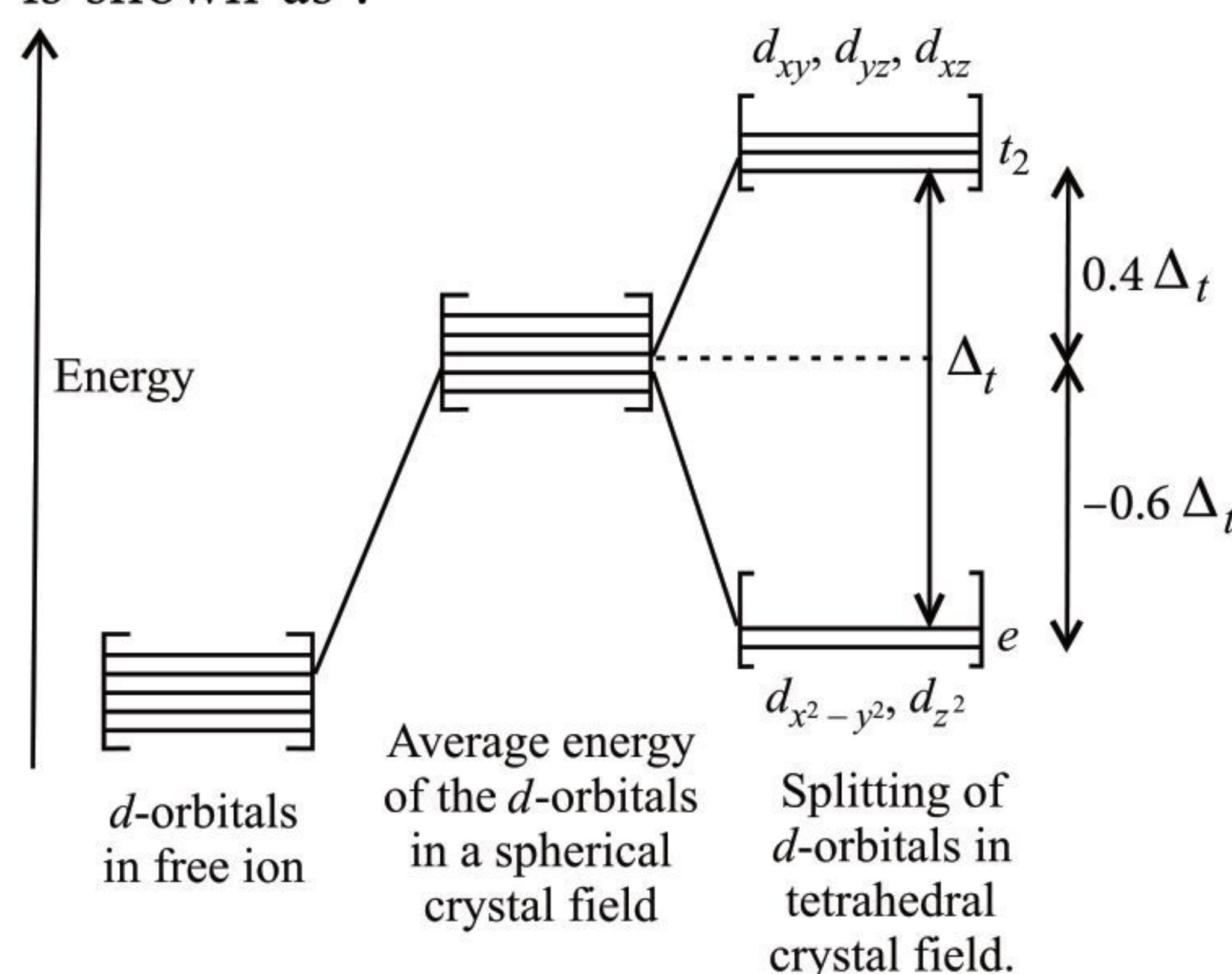
- Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.
- Crystal field splitting in octahedral coordination complexes is shown as :



- If $\Delta_o < P$ (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.
- If $\Delta_o > P$, then pairing of electrons takes place

and a low spin complex is formed.

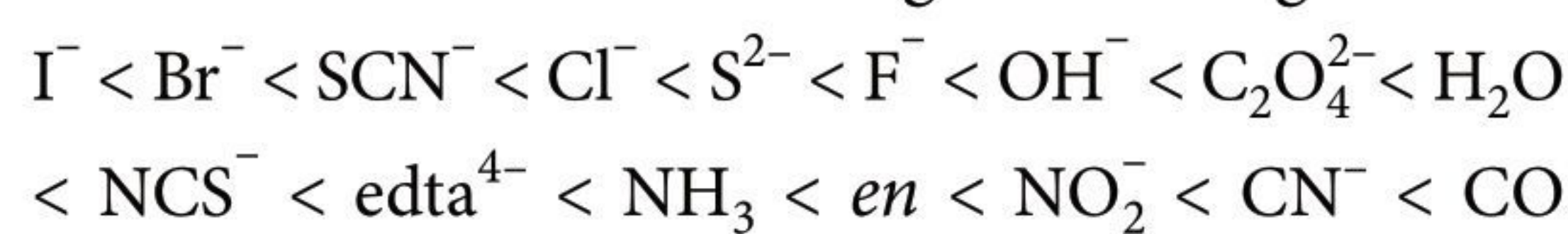
- Crystal field splitting in tetrahedral complexes is shown as :



- Difference in energy between e and t_2 level is less in tetrahedral complexes.

$$\Delta_t = \frac{4}{9}\Delta_o$$

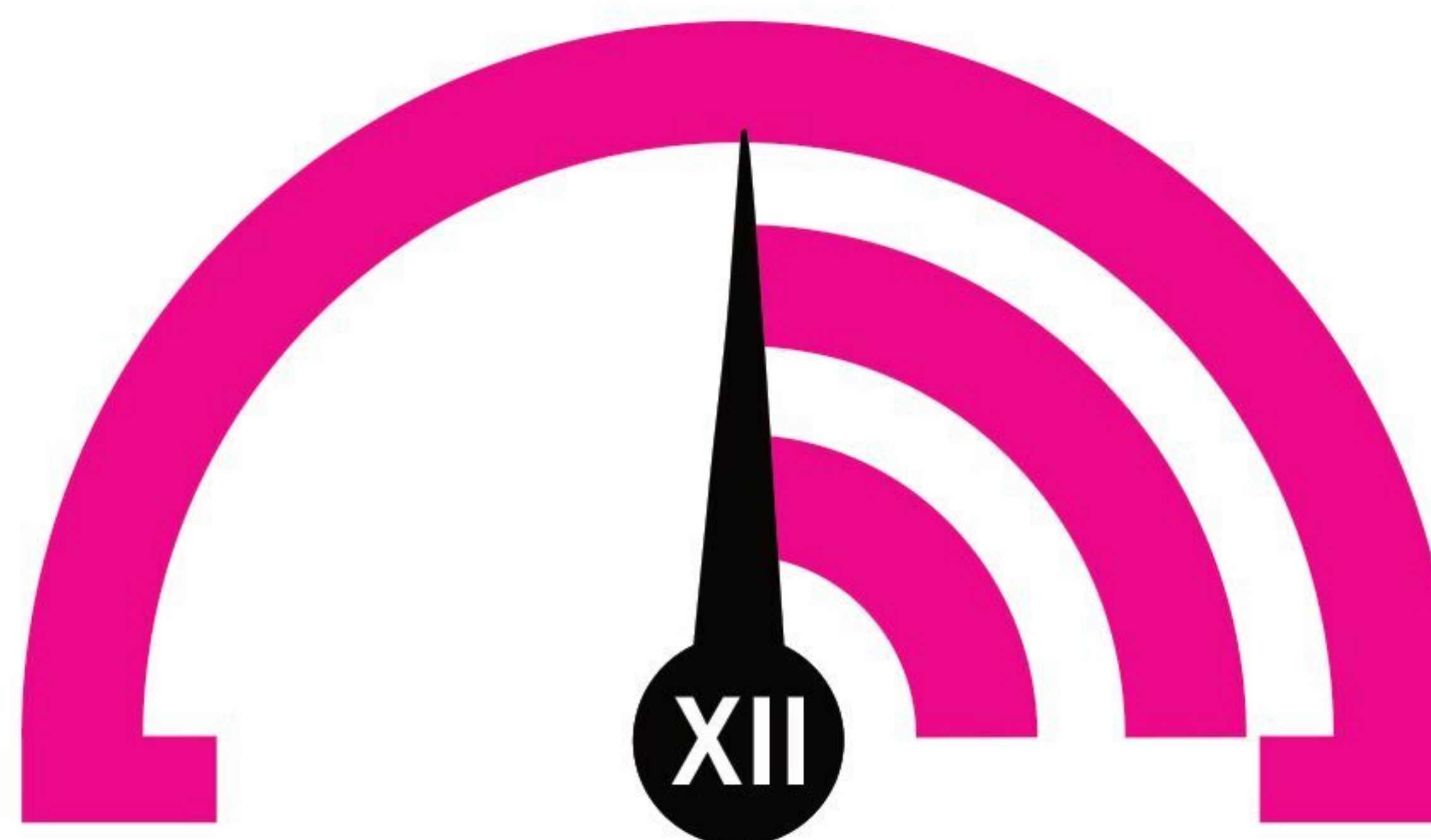
- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength.



- ◆ **Colour of coordination compounds :** The magnitude of CFSE (Δ_o) for most of the complexes is of the same order as the energy of a photon of visible light. Hence, whenever $d-d$ transition takes place, it imparts colour to the complex. The colour of the complex is the colour complementary to the wavelength absorbed.



MONTHLY TEST DRIVE



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks : 120

Solid State | Solutions

Time Taken : 60 Min.

NEET

Only One Option Correct Type

- When light strikes a photographic (AgBr) paper, silver atoms move in through these defects to
 - form negative images
 - form tiny clumps of silver atoms
 - form a colour image
 - none of the above.
- In orthorhombic, the values of a , b and c are respectively 4.2 Å, 8.6 Å and 8.3 Å. Given the molecular mass of the solute is 155 g mol^{-1} and density is 3.3 g/cc , the number of formula units per unit cell is
 - 2
 - 3
 - 4
 - 6
- Two aqueous solutions A and B, are separated by a semi-permeable membrane. The osmotic pressure of solution A immediately begins to decrease. Which of the following statements is true?
 - The solvent molecules are moving from the solution of higher osmotic pressure to that of lower osmotic pressure.
 - The initial osmotic pressure of solution B is greater than that of solution A.
 - Solvent molecules are moving from solution B into solution A.
 - Both (a) and (b).
- The freezing point of equimolar aqueous solutions will be highest for
 - $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ (aniline hydrochloride)
 - $\text{Ca}(\text{NO}_3)_2$
 - $\text{La}(\text{NO}_3)_3$
 - $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose)
- For an ionic crystal of the general formula A^+B^- and co-ordination number 6, the radius ratio will be
 - greater than 0.73
 - between 0.73 and 0.41
 - between 0.41 and 0.22
 - less than 0.22.
- In a mixture, A and B components show negative deviation as
 - $\Delta V_{\text{mix}} = +\text{ve}$
 - $\Delta H_{\text{mix}} = -\text{ve}$
 - A—B interaction is weaker than A—A and B—B interactions
 - none of these.
- If in diamond, there is a unit cell of carbon atoms as fcc and if carbon atom is sp^3 hybridised, what fractions of voids are occupied by carbon atoms?
 - 25% tetrahedral
 - 50% tetrahedral
 - 25% octahedral
 - 50% octahedral
- For a dilute solution, Raoult's law states that
 - the lowering of vapour pressure is equal to the mole fraction of solute
 - the relative lowering of vapour pressure is equal to the mole fraction of solute
 - the relative lowering of vapour pressure is proportional to the amount of external pressure applied
 - the vapour pressure of the solution is equal to the mole fraction of solvent.
- Atoms of element B form hcp lattice and those of element A occupy two third of tetrahedral voids. The formula of compound is
 - A_4B_3
 - AB_2
 - AB_3
 - AB
- In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in
 - lowering of boiling point
 - reducing viscosity
 - reducing specific heat
 - lowering of freezing point.
- In which of the following crystals alternate tetrahedral voids are occupied?
 - NaCl
 - ZnS
 - CaF_2
 - Na_2O

12. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is

(a) 128 (b) 488 (c) 32 (d) 64

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** One molar aqueous solution is more concentrated than that of 1 molal aqueous solution.

Reason : Molarity is a function of temperature as volume depends on temperature.

14. **Assertion :** Solids having more F-centres possess intense colours.

Reason : Excess of Na^+ in NaCl solid having F-centres makes it appear to pink.

15. **Assertion :** The solutions which show large positive deviations from Raoult's law form maximum boiling azeotropes.

Reason : 95% aqueous solution of ethanol is maximum boiling azeotrope.

JEE MAIN / JEE ADVANCED

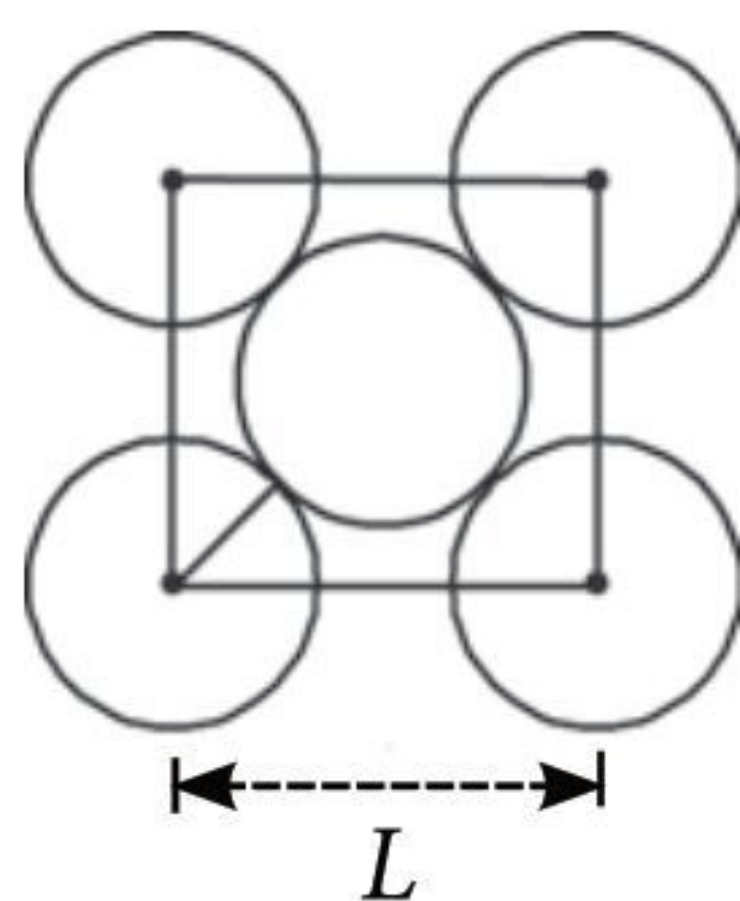
Only One Option Correct Type

16. How much amount of KCl must be added to 1 kg of water so that the freezing point is depressed by 2 K? (K_f for water = $1.86 \text{ K kg mol}^{-1}$)

(a) 40 g (b) 20 g (c) 10 g (d) 60 g

17. The packing efficiency of the two-dimensional square unit cell shown below is

(a) 39.27%
(b) 68.02%
(c) 74.05%
(d) 78.5%



18. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solution in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$)

(a) 724 (b) 740 (c) 736 (d) 718

19. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g?

[Atomic masses : Na = 23, Cl = 35.5]

(a) 2.57×10^{21} (b) 5.14×10^{21}
(c) 1.28×10^{21} (d) 1.71×10^{21}

More than One Option Correct Type

20. The correct statement(s) regarding defects in solids is/are

- (a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
(b) Frenkel defect is a dislocation defect or stoichiometric defect.
(c) trapping of an electron in the lattice leads to the formation of F-center
(d) Schottky defects have no effect on the physical properties of solids.

21. Which of the following are not true about the voids formed in three dimensional hexagonal close packed structure?

- (a) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer.
(b) All the triangular voids are not covered by the spheres of the second layer.
(c) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap.
(d) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer.

22. The solutions which are isotonic with 6% (w/V) solution of urea are

- (a) 18% (w/V) solution of glucose
(b) 0.5 M solution of BaCl_2
(c) 1 M solution of sucrose
(d) 1 M solution of acetic acid.

23. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)

- (a) ΔG is positive (b) ΔS_{system} is positive
(c) $\Delta S_{\text{surroundings}} = 0$ (d) $\Delta H = 0$

Integer / Numerical Value Type

24. A solid compound AB has NaCl structure. If the radius of the cation is 100 pm (picometre), what is the radius (in pm) of anion (B^-)?

25. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.8 bar.

26. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3} . The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{\text{solute}}}{MW_{\text{solvent}}} \right)$, is

Comprehension Type

General naturally occurring solids have definite crystalline shapes which can be recognised easily. There are many other solid materials which exist as powders or agglomerates of fine particles and appear to be amorphous. But when an individual particle is examined under a microscope, it is also seen to have a definite crystalline shape.

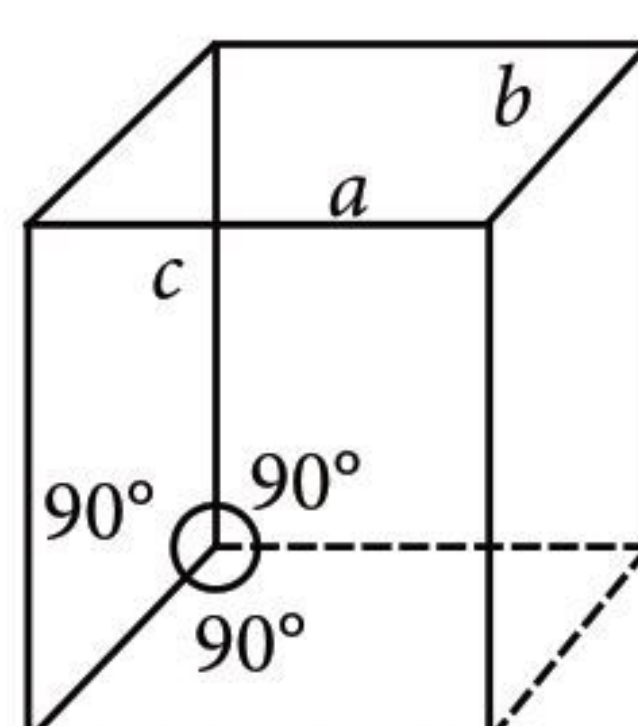
The size of a crystal depends on the rate at which it is formed, the slower the rate, the bigger the crystal.

Crystal system is a method to classify the substance on the basis of their unit cells. On the basis of primitives or axial distance (a, b, c) and interfacial angle (α, β, γ), there may be only seven unique, basic crystal systems. In these crystal systems each unit cell is primitive (*i.e.*, constituents are present only at the corners), so seven crystal systems represent the seven primitive unit cells.

27. TiO_2 is well known example of
 (a) triclinic system (b) tetragonal system
 (c) monoclinic system (d) none of these.

28. The unit cell with the structure given refers to ____ crystal system.

- (a) cubic
 (b) orthorhombic
 (c) tetragonal
 (d) trigonal



Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column-I	Column-II
A. Zinc blende has a hexagonal close packed structure.	p. The crystal has coordination number 6.

B. Wurtzite has cubic close packed structure.	q. In crystal space occupancy is nearly 74%.
C. The crystal having an fcc structure and maintaining equal numbers of cation and anion vacancies.	r. The crystal has alternate tetrahedral void.
D. Anisotropic properties	s. The crystal has the coordination number 4 and possesses Frenkel defect.

- (a) A – q, r, s; B – q, r, s; C – p, q; D – p, q, r, s
 (b) A – q, r, s; B – p, q, r; C – p, q, r; D – p
 (c) A – p, q, r; B – q, r, s; C – p, q, r; D – p
 (d) A – p, q; B – q, r; C – p, q; D – s

30. Match the entries listed in Column I with appropriate entries listed in Column II.

Column-I	Column-II
A. The vapour pressure of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is greater than the vapour pressure of the atmosphere.	p. Isotonic solutions
B. The vapour pressure of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is lesser than the water vapour pressure of the atmosphere	q. Not isotonic solutions
C. 10% glucose (mass/V) and 10% urea (mass/V) solutions are	r. Deliquescence
D. 34.2% sucrose (mass/V) and 6% urea (mass/V) solutions are	s. Effervescence

A	B	C	D
(a) p	q	s	r
(b) r	q	p	s
(c) r	q	s	p
(d) p	q	r	s



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 No. of questions correct
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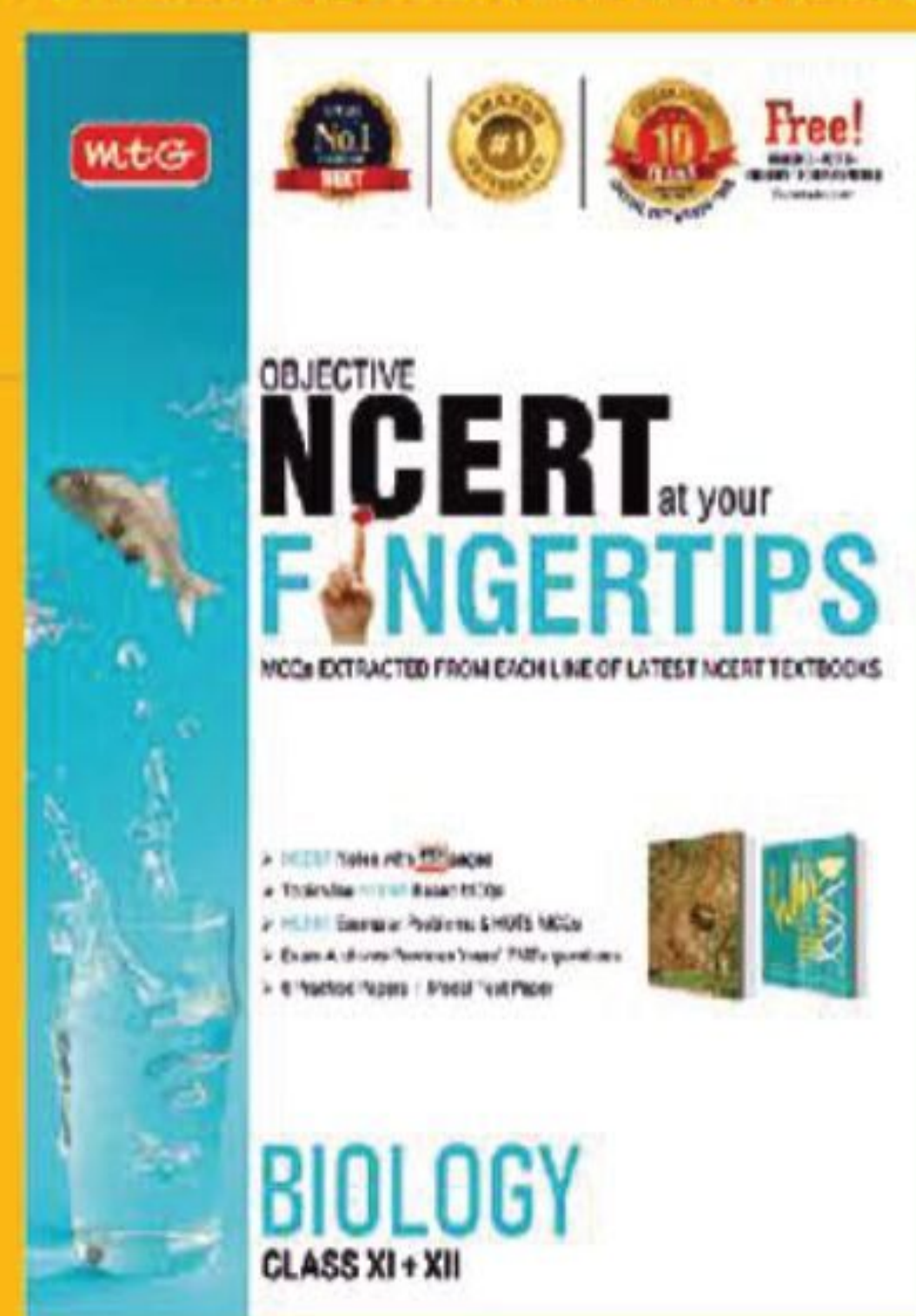
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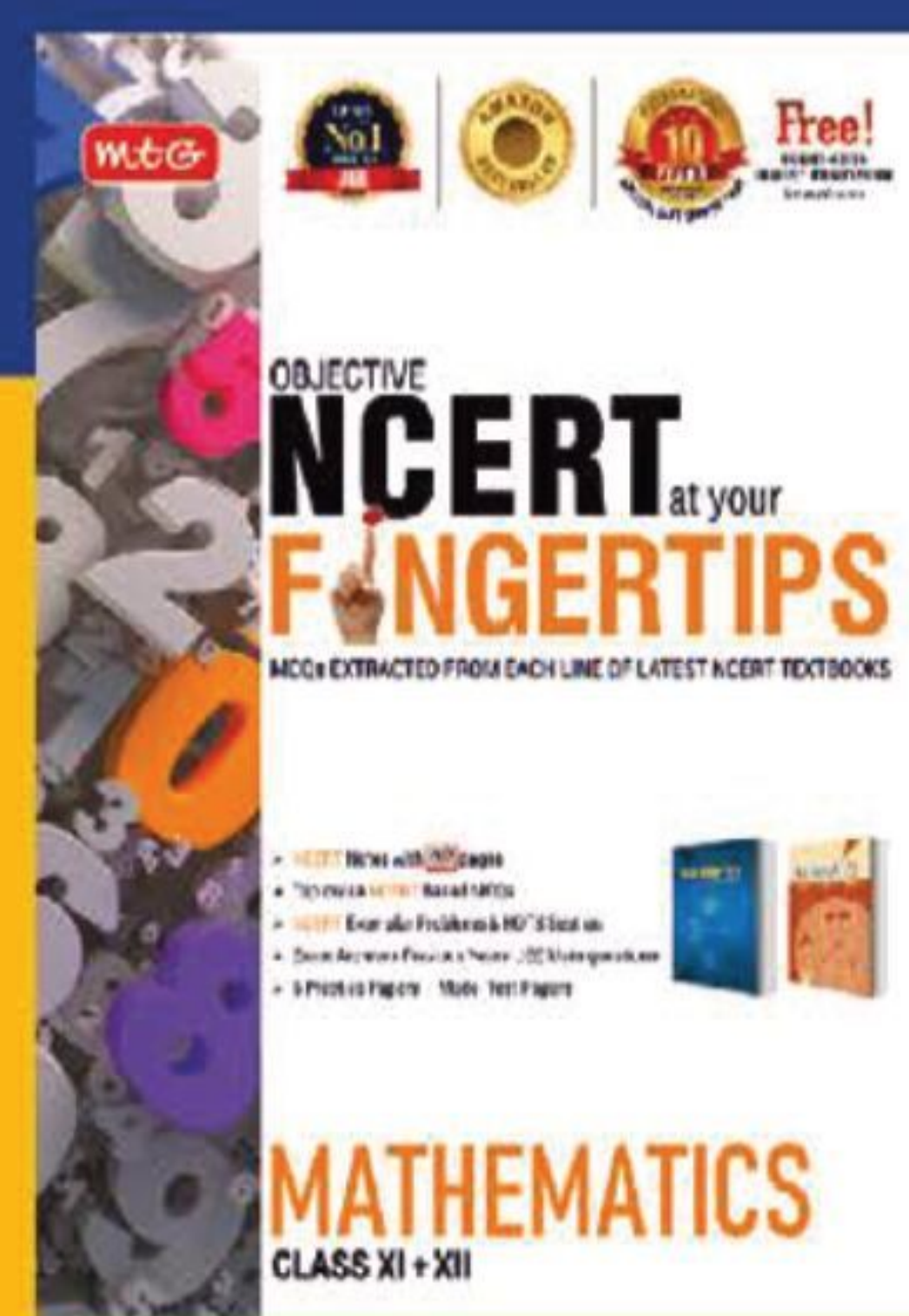
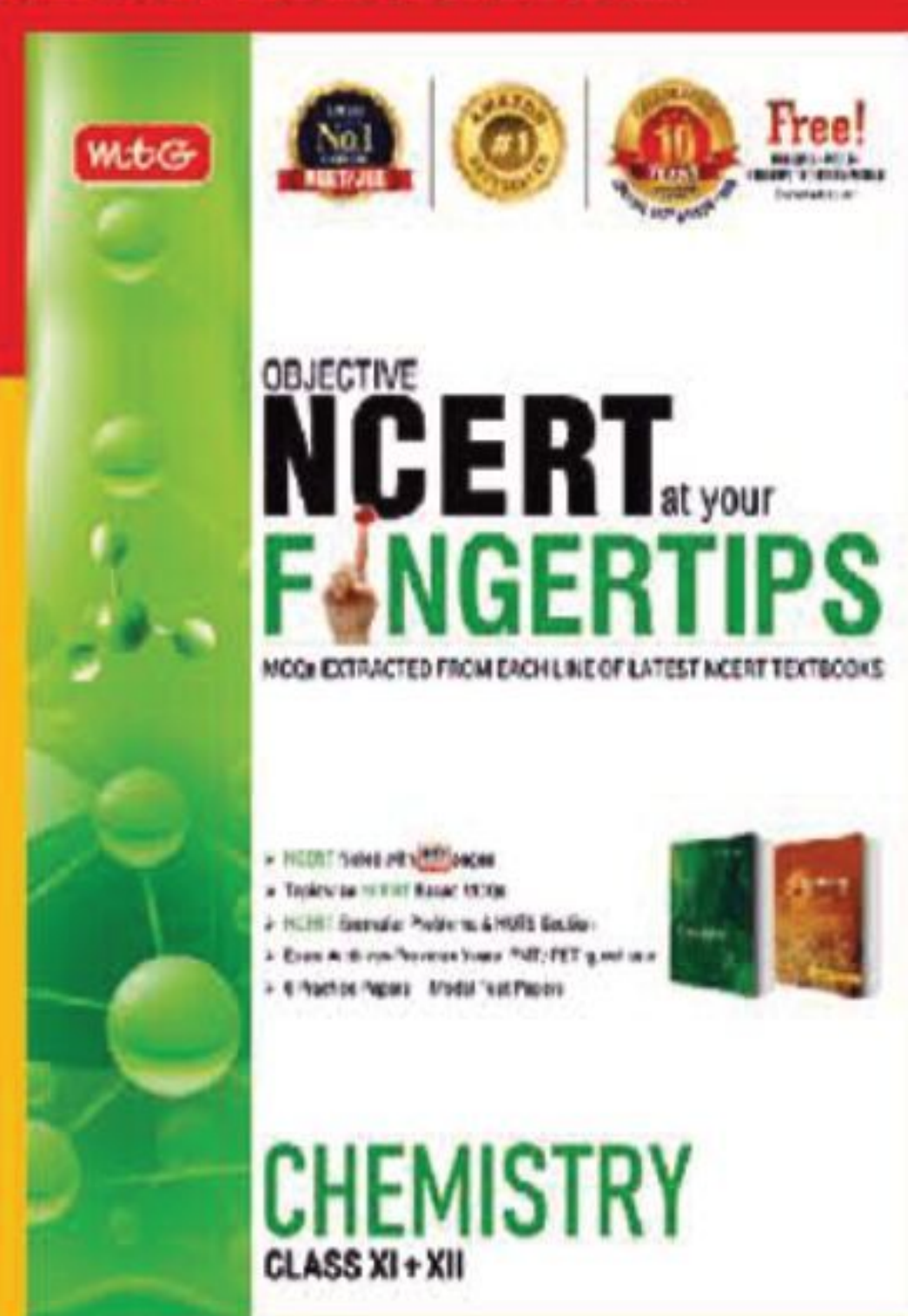
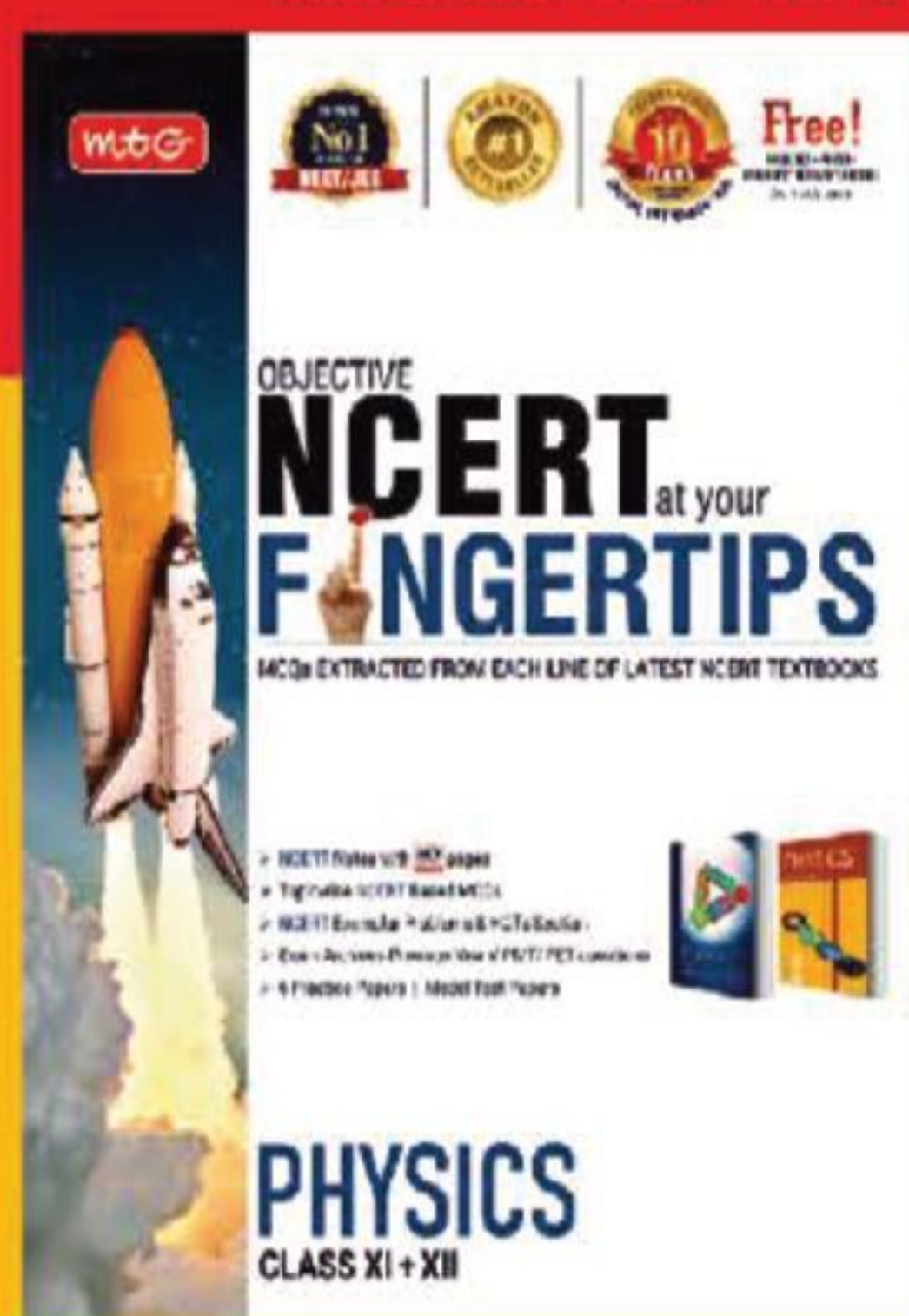
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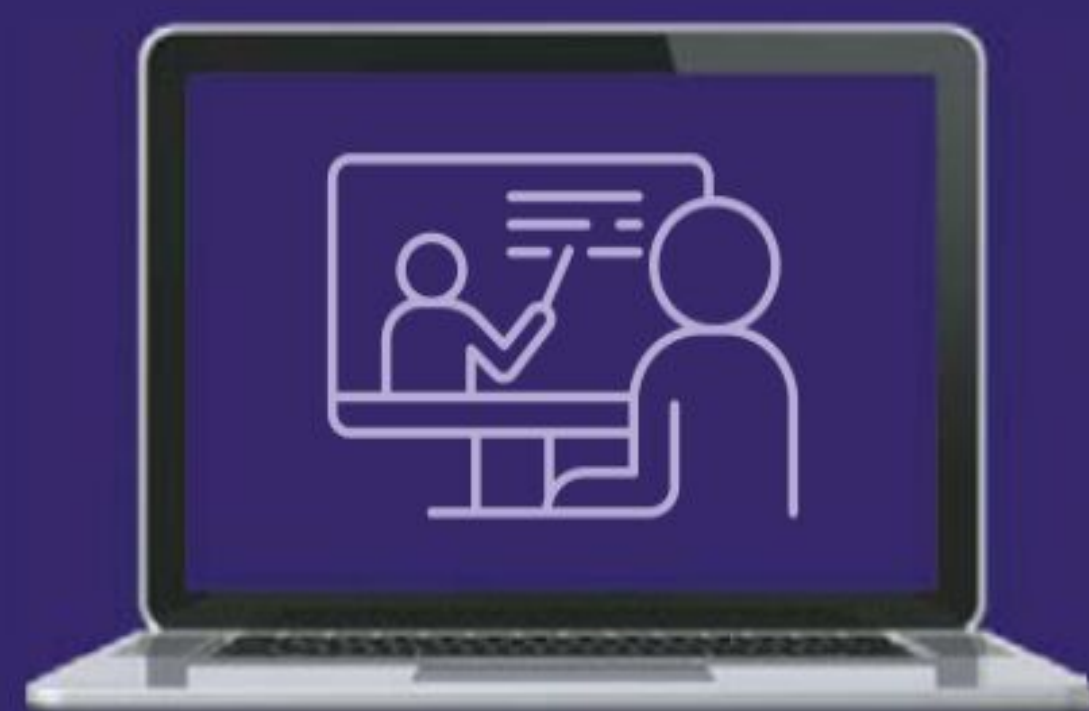
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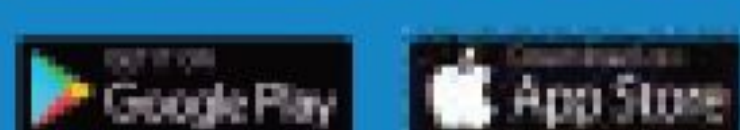
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